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TEXTBOOK OF QUANTITATIVE ANALYSIS

TEXTBOOK OF QUANTITATIVE ANALYSIS

BY

WILLIAM THOMAS HALL

Professor Emeritus of Analytical Chemistry at the Massachusetts Institute of Technology

THIRD EDITION

CENTRAL FOOD TECHNOLOGICAL RESEARCH INSTITUTE, * MYSORE. *
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PREFACE TO THIRD EDITION

This book has now been in constant use at the Massachusetts Institute of Technology for ten years in the author's classes and many of the changes made were suggested by contacts with the students. Professor H. W. Rogers has also examined the manuscript and kindly suggested some changes. A schedule of the work usually carried out by the students has been added which should be helpful to new users of the book.

Under *Acidimetry* the table of acid-base indicators has been revised and an attempt made to bring the theory of the color change up to date. Brönsted's theory of acids and bases is discussed and applications of the theory illustrated, although the text as a whole is not written in terms of the theory, for which reasons are given.

Under *Oxidation and Reduction* an explanation of the theory of oxidation-reduction indicators is given and their use is illustrated.

Under *Gravimetric Analysis* the discussion of colloidal solutions, aging of precipitates, coprecipitation, and post precipitation has been introduced. In Part I, the number of problems has been increased by about twenty per cent. Some new illustrations and some new procedures have been added. A few of the older procedures have been dropped as well as some of the old illustrations.

In Part II of the book there have been numerous improvements, and under *Steel Analysis* an attempt has been made to describe well-known methods as carried out today by the chemists of the U. S. Steel Corporation or of the National Bureau of Standards. Under electrometric methods of analysis, some of the details in manipulation are omitted because numerous forms of apparatus are now on sale and the makers of the various instruments supply full directions for their use. The theory of the glass electrode, however, is discussed briefly.

With respect to electrode potentials, the values are now given in terms of *oxidation potentials*, rather than *reduction potentials*, which means that all the signs are changed in the mathematical expressions. Considerable unnecessary confusion has resulted from the fact that in the United States many of our best physical chemists prefer to call an electrode potential *positive* which chemists of other countries and all physicists call *negative*. When the chemist says that the positive-to-negative direction in a Bunsen cell is from the zinc to the copper he is thinking of the current passing through solution, and when the physicist says that copper is positive to zinc in the Bunsen cell he is thinking of the current passing through the wire. Both are right, but when students are studying chemistry and physics at the same time it is less confusing when the chemist and the physicist both regard phenomena from the same viewpoint and use the same signs in their mathematical expressions. Moreover, all English books and the majority of the best books printed in the United States on analytical chemistry have now conformed to the nomenclature established by the physicists.

WILLIAM T. HALL

CAMBRIDGE, MASSACHUSETTS
May, 1941

PREFACE TO FIRST EDITION

Nearly thirty years ago, the writer of this book translated F. P. Treadwell's " Kurzes Lehrbuch der analytischen Chemie." Treadwell, although himself an American, was at that time teaching at Zürich, and the book represented his lectures on analytical chemistry and the methods which he had tested with his students. It was meant to be a *brief* text written especially for students.

After the book was published, Treadwell naturally had his students test many of the new analytical procedures that were proposed from time to time and added many of them to his text. The translator did the same thing, until finally the English translation became about twice as large as it was at first and chemists began to look upon it as a reference book rather than a brief text for students. Moreover, to avoid unnecessary repetitions, there were many cross references which made it less convenient for students to use in the laboratory. Finally, in 1928, the suggestion was made that the book be reduced to its original size.

This idea of again making the book a brief text adapted to the needs of sophomores in our colleges and technical schools did not appeal to the publishers. They preferred to publish such a text independently. The present book is the result.

Those familiar with the Treadwell book in the form of its English translation will note at once that the greater part of the procedures here given are practically identical with those of the older book although the similarity to the original text of Treadwell is not so striking.

The present book represents a course in analytical chemistry as given at the Massachusetts Institute of Technology to embryo chemical engineers. For these students, the excellent text of H. P. Talbot was formerly used and it will be noted that the subjects selected include the methods given in that text which, however, represented work usually accomplished by students in one semester whereas this book represents the work of two semesters.

One feature of the book, which was also adopted by Dr. Talbot at the suggestion of the writer, is that titration methods are given first. Practical experience has shown that students accomplish more work and get more out of the course when this is done. This fact was discovered quite by accident but verified by careful observation in three laboratories under some five or six different instructors.

The teacher of analytical chemistry is obliged to turn in grades for all of his students. Acting on the principle that any measurement is more likely to be correct when based upon many observations the writer has tried to work out a scheme for grading the students which will be based upon as many observations as possible and practically free from personal feelings toward the individual members of the class. The students are told exactly how the grades are made, and an explanation is always given whenever a student feels that the grade is not fair. At the Massachusetts Institute of Technology we are asked to turn in at the end of each semester a single grade for the entire work covered. Just how much weight should be given to laboratory work, how much to faithful performance of home work assigned, and how much to records made in written examinations, is left for the instructor to determine. The writer makes out grades on a percentage basis for the laboratory work, the weekly quizzes, and for the problems assigned for home work. Then a composite grade is made counting the laboratory work 40 per cent, the class work 50 per cent, and the home problems 10 per cent. Just a word as to how these grades are prepared.

In the laboratory, the student is asked to report the results he obtains as soon as possible. Each result is graded on a scale of 10, taking into consideration the neatness of the notebook, the accuracy of the result, and the agreement of checks. At the end of the term the grades thus obtained are added up and divided by a number such that the average student working exactly the time assigned will obtain a quotient of 60 and only a few students will obtain quotients better than 90. These quotients are called the laboratory grades. The class meets in the lecture room two or three times each week and at one of these exercises a 30-minute written quiz is given with particular emphasis placed upon stoichiometric problems and the ability to balance equations representing chemical reactions. Each of these quizzes is graded on a scale of 10 and the classroom grade determined by multiplying the average grade by 10. It has been found inadvisable to give a final examination unless time is given for the student to make an adequate review of the subject. The grade for problems done at home is based upon the number of correct solutions and the number of problems assigned. In this book a set of problems for home work is given at the end of each chapter, and about 200 problems are assigned during the entire sophomore year. It works best not to give the answers in the book. Some students, to be sure, keep a record of the correct answers and pass them along to their fraternity brothers, but most of the students realize that they had best try to do the work independently and those students having the correct solutions often spend a good deal of time explaining them to others, which is good for all concerned.

The laboratory is kept open about eight hours a day, and the student is encouraged to do extra work and, in order to develop as far as possible the spirit of research, the better students are usually assigned some simple research problem to work out and report on. The writer has on file many excellent reports thus made, and he has himself obtained a great deal of valuable information by trying out new procedures with his students.

William T. Hall.

Massachusetts Institute of Technology,
September, 1930.

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SUGGESTED LABORATORY WORK

The following program is suggested for two semesters with at least five hours per week scheduled for work in the laboratory with permission to work as much more as the student desires. It has been found practical to assign six or eight problems a week to be done at home and to give weekly tests. Then a percentage grade can be calculated for the class tests, the problems correctly solved, and the laboratory work accomplished. A composite grade can be calculated with the weights 5, 4, and 1 for class, laboratory, and home work. In the laboratory, the work goes slowly at first, but a total of 225 can be called 100 per cent with each item graded on a scale of 10 except those marked with an * which can be counted double. In this way, the brilliant student has to do considerable laboratory work and the most skilful analyst has to understand the procedures. On the other hand, the program enables each student to know how he stands at all times and encourages him to keep the work up to date.

First Semester

1. Calibration of a Buret (pp. 28–31).
2. Titration of HCl against NaOH (pp. 67–69).
3. Standardization of NaOH against $KHC_8H_4O_4$ (p. 73).
4. Analysis of an alkali carbonate, assumed to be Na_2CO_3 (p. 75).
5. Analysis of a solid acid, assumed to be $H_2C_2O_4 . 2H_2O$ (p. 77).
6. Iron in an ore by $K_2Cr_2O_7$ (pp. 98–104).
7. Chromium in an ore (p. 104).
8. Iron in an ore by $KMnO_4$ (p. 116).
9. Manganese dioxide in pyrolusite (p. 119).
10. Iodimetric determination of copper in an ore (p. 137).
11. Iodimetric determination of antimony in stibnite (p. 138).
12. Determination of silver with KCNS (p. 147).
13. Determination of halogen by the Volhard titration (p. 148).
14. Gravimetric determination of chlorine in a chloride (p. 191).
15. Gravimetric determination of iron (p. 194).
16. Gravimetric determination of sulfur (p. 197).
17. Determination of P_2O_5 in apatite (p. 204).
18. Determination of " insoluble " and " combined oxides " in limestone (p. 208).
19. Gravimetric determination of CaO (p. 209).
20. Gravimetric determination of MgO (p. 212).
21. *Determination of CO_2 (p. 215).
22. Electrolytic determination of copper (p. 231).
23. Determination of lead in brass (pp. 231, 234).
24. Determination of zinc in brass (p. 233).

Second Semester

1. Any of the above procedures not finished in the first semester.
2. *Calibration of a set of weights (pp. 13–16).

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* Not required of all students.

3. *Determination of SiO_2 in an insoluble silicate with HF correction (p. 238).
4. *Determination of potassium in an insoluble silicate (pp. 241–244).
5. *Determination of sodium, in an insoluble silicate (p. 245).
6. Phosphorus in steel by alkalimetry (p. 252).
7. Phosphorus in steel by another method (pp. 253, 254).
8. Manganese in steel by $NaBiO_3$ (p. 258).
9. Manganese in steel by another method (pp. 260, 261, 262).
10. Nickel in steel (p. 281).
11. Carbon in steel (pp. 269, 275).
12. Chromium in steel (p. 286).
13. Vanadium in steel (p. 286).
14. Sulfur in steel (pp. 290, 291).
15. Tungsten in steel (p. 294).
16. Arsenic in an ore (p. 300).
17. Titanium in an ore (pp. 302, 303).
18. Lead in bearing metal (p. 311).
19. Antimony in bearing metal (p. 312).
20. Tin in bearing metal (p. 313).
21. Sulfur in pyrite (p. 296).

On a scale of 10, the average mark should be about 8, and total credits of 145 (65 per cent of 225) should be sufficient for a clear record. Every student should accomplish enough work to get 115 points, by working diligently five hours a week for fifteen weeks.

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* Not required of all students.

CHAPTER I

INTRODUCTION

The purpose of a quantitative analysis is to determine the relative quantity of one or more constituents of a compound or of a mixture. The methods to be employed depend somewhat upon the nature of the substances analyzed so that, as a rule, a qualitative analysis should precede the quantitative one, or, at least, there should be some knowledge of what elements are likely to be present. The chemical reactions used in quantitative analysis are, for the most part, reactions which are used or can be used as qualitative tests, and the chemical principles involved are the same. In quantitative analysis, however, it is necessary to measure accurately the quantity of sample taken and either the quantity of reagent required to cause a definite reaction to take place or the quantity of one of the products formed by the reaction. Quantitative analysis, therefore, differs from qualitative analysis with respect to the necessity of making careful measurements of materials. Since all chemical research is based upon quantitative analysis, it is clear that the ability to make accurate analyses is one of the most important assets of the chemist irrespective of the field in which he may choose to work eventually.

The most important tool of the chemist is the balance by which weighings are made.[1] The balance used by the chemist combines the physical principles of the lever and the pendulum (Fig. 1.)[2] The *beam*, from which the *scale pans* are suspended, represents a horizontal lever with two arms of equal length. To be serviceable, a balance must be *accurate* and *sensitive*. It fulfills the first condition if (1) the arms are actually of equal length, (2) the point of support (the fulcrum about which the beam rotates) lies above the center of gravity, and (3) the fulcrum (center knife-edge) and the knife-edges from which the pans are suspended lie in the same plane and are parallel to one another.

---

[1] Strictly speaking, the balance determines masses and not weights. The unit of *mass* is the *gram* and the unit of *weight* is the *dyne* in the absolute system. The mass in grams, multiplied by the acceleration of a falling body due to gravity, gives the weight in dynes. At any given place, therefore, the weights are proportional to the masses, so that it is common practice to neglect the value of gravity and speak of a *weight* of so many grams. The masses determined by the chemical balance are independent of the value of gravity whereas a spring balance may not show the same weights for the same masses at different places on the earth's surface.

[2] Reproduced, by permission, from Catalog 8 of Christian Becker, Inc.

The beam of the balance is provided with a long pointer which swings over a fixed scale near the base of the balance case. A small adjustable nut on the pointer, sometimes above and sometimes below the beam, serves to raise or lower the center of gravity of the moving parts and thus change the sensitiveness. At one end of the beam, and in some balances at both ends, is found an adjusting screw which serves to make the effective weights of the arms equal.

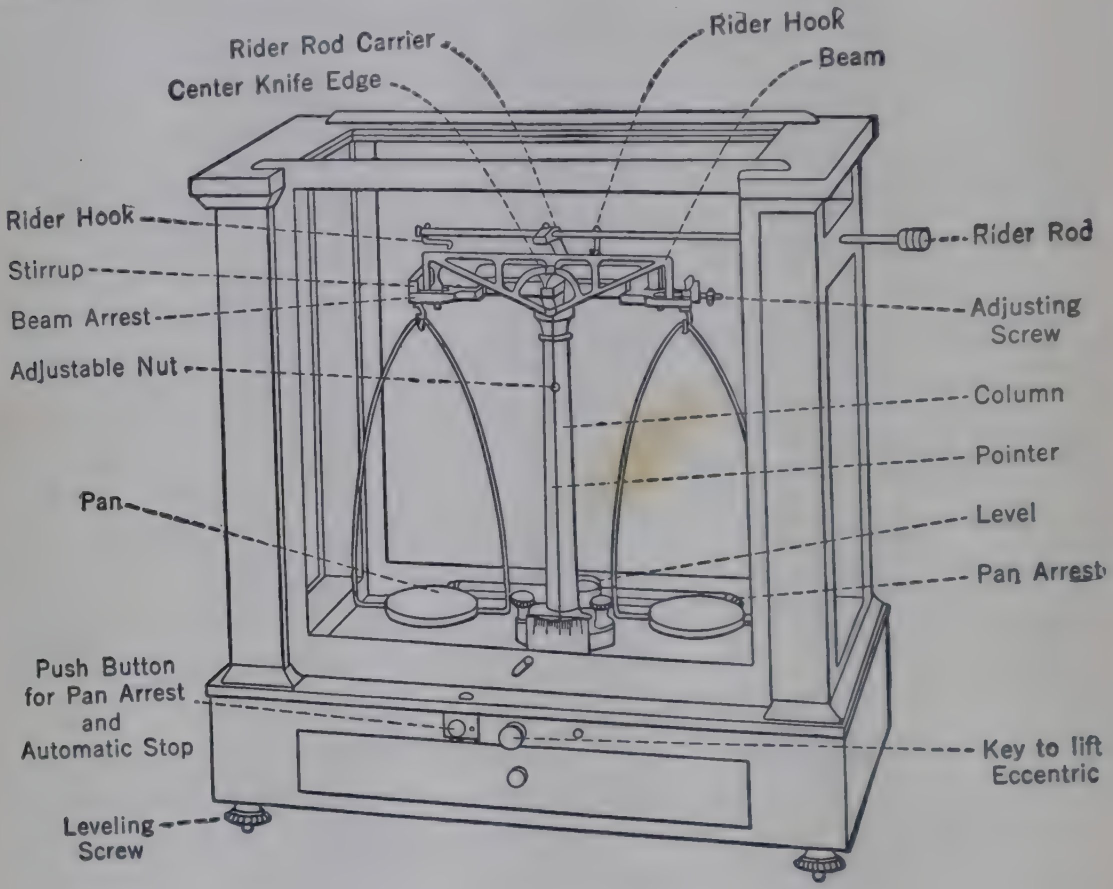
Rider Rod Carrier
Rider Hook
Beam
Center Knife Edge
Rider Hook
Rider Rod
Stirrup
Adjusting Screw
Beam Arrest
Adjustable Nut
Column
Pointer
Pan
Level
Pan Arrest
Push Button for Pan Arrest and Automatic Stop
Key to lift Eccentric
Leveling Screw

Fig. 1.

At the middle of the beam, on the under side, is a knife-edge which is usually made of polished agate. When the balance is in use, this knife-edge rests upon a plate of polished agate so that the beam can swing with very little friction. At the ends of the beam are other knife-edges from which the balance pans are suspended. When not in use, the beam should be raised so that the knife-edges are not in contact with their bearings. This is effected by means of a frame operated by a key at the front of the balance case. By turning the milled head clockwise, the beam is raised. With an equal load in each pan, and the beam resting on the knife-edge, the pointer should swing an equal number of divisions both sides of the zero of the scale when the beam is in motion and should finally come to rest at the zero mark. If a small weight is added to either pan the beam and the pointer will swing through an angle and take up a new position of equilibrium. This new position will be the result of the moments of three effective forces — the weight of the beam and the weights in each pan.

The angle α which the pointer at its new resting place makes with its original position is determined by the excess weight, p, the length of the balance arm, l, the weight of the beam, q, and the distance, d, between the center of gravity and the point of support of the beam. Expressed mathematically,

$$\tan \alpha = \frac{p \cdot l}{q \cdot d}$$

The *sensitiveness*, or *sensibility*, is measured by the angle α when p has a definite weight, usually 1 mg. Since the tangent of a small angle is practically the same as the angle, and the tangents of the angles that the pointer makes are directly proportional to the number of divisions between the two points of rest on the scales, it is customary to regard the sensitiveness or sensibility as *the number of scale divisions that the zero point is displaced by an excess weight of 1 mg.*

It follows, then, that the sensitiveness of a balance is directly proportional to the length of the balance arms and inversely proportional to the weight of the beam and to the distance of the center of gravity below the point of support. It is clear also that the observed deflection is proportional to the length of the pointer.

The conditions for maximum sensitiveness are more or less conflicting. Thus long arms are incompatible with minimum weight. The length of arms is also limited by the fact that, the longer the arms are, the greater the time required for one complete swing of the pointer. The weight of the beam also affects the time of swing in the same manner. On the other hand it is important that the beam should be rigid.

Long arm balances, although sensitive, possess the disadvantage of a long time of swing which renders weighing a tedious process. For moderate loads, short arm balances with light beams of aluminum alloy are sensitive and fast.

It is possible to decrease the time of swing by lowering the center of gravity, but this makes the balance less sensitive. For ordinary work, it is well to adjust the sensitiveness so that 1 mg excess weight will displace the zero point about five scale divisions with light loads. The center of gravity must always be below the knife-edge or the balance will be in neutral or unstable equilibrium.

Precautions in the Use of a Balance

1. The balance should rest upon a firm support which is practically free from mechanical vibration. Direct sunlight should not fall upon the balance as it will cause irregularities and errors in weighing.

2. When not in use the balance beam should always be raised off the knife-edges as otherwise these are likely to be injured by jarring.

3. The beam should always be lowered slowly and carefully.

4. The beam should never rest upon the knife-edge while weights or substances are being added to or removed from the pans.

5. The beam may be set swinging by dropping the rider upon the beam or removing it for a moment. It may also be set in motion by fanning one pan gently with a motion of the hand, but in no case should motion be started by touching the pan or by suddenly lowering the beam upon its knife-edge.

6. All weighings should be made methodically, with the weights tried one after another in their proper order.

7. Before making a weight, the adjustment should always be tested. The balance is properly adjusted (*a*) when it is level, (*b*) when the pointer rests at the zero mark with the beam raised, (*c*) the pointer swings equal distances on either side of the zero when the beam is set in motion with no load in the pans.[1] If the balance has pan arrests which work independently of the mechanism that lowers the beam, these arrests should be adjusted so that the pointer is at the zero mark when the beam is on its knife-edge and the pan arrests are in place.

8. Final adjustment with the rider and all observations regarding the swing of the pointer should be made with the balance case closed to prevent errors arising from air currents. When the balance is left, the case should always be closed.

9. The weight of a substance should be recorded, *first*, by adding up the weights missing from the box (in which every weight should always have its own place), and *second*, by adding up the weights that are on the pan. After the final weight has been made, it is convenient to make this second addition when the weights are being returned to the box. By always checking the weights as a matter of habit, serious errors are often avoided.

10. Substances to be analyzed should never be placed directly upon the balance pan but on a watch glass or in a tube. The object should not be warmer or colder than the air in the balance case. Air currents

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[1] Some workers prefer to adjust the balance so that the pointer rests three or four divisions to the right with no load in either pan. Cf. Brinton, *J. Am. Chem. Soc.*, **41**, 1151 (1919).

from a hot body make it weigh too little, and condensation of moisture on a cold body makes it appear too heavy.

11. Care should be taken not to overload the balance.

A separate set of weights should be provided with each balance. In analyzing a given material, the chemist is required to determine the weight ratios of the various constituents. He reports the percentage of iron present rather than the weight. It is important, therefore, that the weights in any set should stand in the proper relation to one another and relatively unimportant whether the 10-g corresponds exactly to the 10-g weight in some other set. In analyzing ores for precious metals, it is customary to weigh out a large sample on a " pulp balance " which need not be sensitive to 1 mg. The analysis is finished by weighing a very small fragment of metal on a " button balance " sensitive to $\frac{1}{100}$ mg. Ordinarily, however, all the weighings used in any chemical analysis should be made with the same balance and the same set of weights. If a weight is lost or misplaced, a new weight should always be tested to see if it bears the proper relation to the other pieces in the set.

Sets of weights used in chemical analysis usually contain a 50-g weight and sometimes a 100-g weight. Sometimes the smallest weight is 1 mg, but a set need not contain any weight smaller than 5 mg. The numbers on the weights indicate grams when the value is 1 g or over and milligrams if the weight is a fraction of a gram.

Weights smaller than 10 mg are usually obtained by the use of a " rider " or small piece of aluminum wire which may be shifted to various positions on the beam of the balance. The manner in which the beam is divided varies with different makes of balances. When the rider is placed directly over the knife-edge that supports the right pan, it indicates its true weight; and when it is placed at a fraction of the distance between middle and outer knife-edges, it indicates that fraction of its true weight. Riders as a rule weigh 5, 6, 10, or 12 mg. Balances which are made so that the rider can be placed directly over the pan suspension usually take a 10-mg rider or a 5-mg rider. Balances which are made with the top of the beam rounded off at the ends usually take a 12- or 6-mg rider. The larger divisions on the beam graduations are always 1 mg apart when the proper rider is used. The smaller subdivisions are either tenths or fifths of a milligram.

The *chainomatic balance* does not require a separate rider. One end of a small gold chain is fastened to the balance beam and the other end to a hook which can be moved up and down a vertical scale. This hook is operated by a milled head outside the balance case on the right. Movement of the hook changes the weight of chain that is supported by the beam so that the positions on the scale correspond to milligrams. This may be adjusted while the balance is in motion.

The magnetically damped balance is useful for rapid and accurate weighings. It is equipped with an aluminum vane suspended from the beam and hung between the poles of a fixed magnet. As the beam swings, induced currents are set up and a magnetic field produced which opposes the motion of the swing so that the beam is quickly brought to rest.

In air-damped balances, large hollow cylinders, closed at the bottom, are fixed just below each stirrup which holds the pans. Inside these cylinders are smaller cylinders suspended from the stirrups. As the balance moves, the smaller cylinders move, and the displacement of the air causes the damping.

Methods of Weighing

It is important to keep the pans, beam, bearings, and all parts of the case clean and free from dust and chemicals. Before starting to weigh, see that the balance is properly adjusted, and determine the *zero point* and the *sensibility* or *sensitiveness.* If necessary, turn the leveling screws at the base of the case until the spirit level back of the pillar shows the correct position. Note also whether the knife-edges are in the proper positions with respect to the bearings and whether the pointer rests at the zero point of the scale. Lower the beam rest, by slowly turning the knurled knob at the bottom of the case in an anti-clockwise direction,[1] and see that the pointer is still at the zero point when the pans are resting on the pan rests, making the proper adjustments, if necessary. Then with the balance case closed, release the pan rests and see that the pointer is quiet or moves back and forth to equal distances on both sides of the zero mark. If necessary, move the adjustment screw on the end of the beam, but it is better to allow for a slight zero error, when it is not more than one scale division, than to make frequent adjustments.

The pointer swings as a pendulum and, owing to air resistance, is subject to a damping, or shortening of the swing, and unless the eye is exactly in alignment, there is a parallax error in reading the position of the pointer on the scale. The halfway point is best determined by taking the halfway point of two or more complete swings. A complete swing of a pendulum involves a return to the starting place, and the measurements will represent complete swings if the final reading is taken on the same side as the initial reading so that there will be one more reading on one side than the other (see *Weighing by Swings*). If the center knife-edge is sharp so that there is little friction to overcome save that of the air, the damping will be slight, and negligible if the swing is made short; therefore for ordinary work it is sufficient to take the halfway point of a halfswing, with each turning point less than five scale divisions from the zero mark. With these short swings, moreover, there is less danger of parallax errors than with long swings.

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[1] In putting anything on the balance pan or taking anything off, the balance beam should always be supported and not resting on the central knife-edge.

After taking the zero reading, the next thing is to determine the sensibility or *number of scale divisions that the zero point is displaced by a load of 1 mg*. The sensibility varies with the load,[1] but it is well to know how sensitive the balance is at the start because this knowledge will help the operator to make rapid weighings.

Rapid Method. For ordinary work, it is convenient to adjust the center of gravity by means of the adjusting nut on the pointer, so that a load of 1 mg will make the pointer have an initial swing of at least five scale divisions to the left when the pan rests are carefully released. In weighing, note the initial swing when the rider indicates within 0.5 mg of the correct weight. Then change the position of the rider so that the initial swing is a little to the other side of the zero line, and note the new swing; from these two readings estimate where the rider should be to give no swing. This method of making two trials on both sides of the true weight is more rapid and more accurate than attempting to place the rider where the swings will be exactly the same as in making the zero reading. For very precise work, however, weights should be made by the *method of swings*, and corrections should be made for balance-arm error and for buoyancy due to air. The weights should be carefully calibrated.

Single Deflection Method. Adjust the balance so that the pointer swings three or four divisions to the right when the pan support is released and rests on this side of the zero reading on the scale. In weighing, add weights until this same deflection is obtained on releasing the pan support. This method of weighing is rapid but is inapplicable to a balance which has a single release operating both beam and pan supports.[2]

---

[1] This is because the center of gravity changes with the load. How this changes depends upon whether the three bearings lie in the same plane or not. As a rule, the sensibility is lowered by increasing the load in the balance pans, partly because the beam becomes slightly distorted and the center of gravity is lowered, but if the three bearings are exactly in the same plane, and the beam is absolutely rigid, the center of gravity will rise, but never reach the level of the middle knife-edge, so that increasing the load will then increase the sensibility.

[2] Brinton, *J. Am. Chem. Soc.*, **41**, 1151 (1919).

Method of Swings. First of all determine the zero-reading of the balance by setting the beam in motion (without any load in either pan), observing and recording the turning points, or extreme positions, of the pointer on the scale of an even number of complete swings, and take the mean of the readings. The first complete swing may be inaccurate on account of the jar in shutting the balance door, etc. Remember that a complete swing starts and ends on the same side, so that for any number of complete swings an odd number of readings must be taken. In order to give the same algebraic sign to all the observed readings it is well to number the divisions on the scale from left to right from 0 to 20 so that the zero point in case both balance arms are of equal length and weight will be numbered 10. It is to be noted that the zero reading (the point of the scale at which the pointer rests when the balance is in equilibrium with nothing in either scale pan) may change during the course of the day, and disregard of this fact may lead to a considerable error. The cause of the displacement of the zero reading is that the first condition for the accuracy of a balance is not fulfilled; on account of unequal warming the arms become of unequal length.

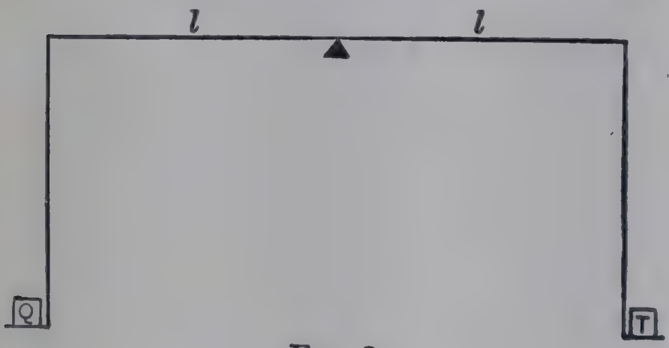

FIG. 2.

The next thing to be determined is the sensitiveness of the balance for the object to be weighed. For this purpose place the object in the left balance pan and weights in the right pan until equilibrium is established as nearly as possible, and determine the rest point of the pointer on the scale in the same way that the zero reading was made above. Add or remove an additional weight of 1 mg by means of the rider, and determine the rest point again.

The difference (*d*) between this and the previous point of rest gives the sensitiveness of the balance. Assuming the zero reading to lie at 10.22, the first rest, obtained with a load of 19.723 g, to be at 9.80, and the rest point with a load of 1 mg less (with a load of 19.722 g) to lie at 12.32, then the sensitiveness of the balance will amount to 12.32 − 9.80 = 2.52 scale divisions.

As the zero reading of the balance was at 10.22 and the rest point with a load of 19.723 g was 9.80, it follows that the object was lighter than the weights in the right-hand pan, and in fact the excess of weights in the pan was sufficient to move the point of rest 10.22 − 9.80 = 0.42 of a division on the scale. This amount can be calculated from the determination of the sensitiveness of the balance as follows:

Since 2.52 of the scale divisions correspond to 1 mg, then 0.42 of a scale division corresponds to 0.42 ÷ 2.52 = 0.17 mg, or about 0.2 mg.

The true weight of the body in air is consequently 19.723 − 0.0002 = 19.7228[1] g.

In making a weighing one should always accustom himself to note the observations methodically, as follows:

Assume that a platinum crucible is to be weighed.

Zero Reading		I. Rest Point with Load of 12.052 g		II. Rest Point with Load of 12.053 g	
Left	Right	Left	Right	Left	Right
4.2	17.6	5.8	18.7	3.5	15.8
4.6	17.1	6.2	18.3	3.8	15.4
5.1	....	6.6	....	4.2	
Sum = 13.9	34.7	18.6	37.0	11.5	31.2
Mean = 4.63	17.35	6.2	18.5	3.83	15.60
....	4.63	....	6.2	....	3.83
Sum of both means = 21.98		....	24.7	....	19.43
Mean = 10.99		....	12.35	....	9.71

Sensitiveness = 12.35 − 9.71 = 2.64 scale divisions.
12.35 − 10.99 = 1.36 scale divisions.
1.36 ÷ 2.64 = 0.5 mg.
Weight of crucible = 12.052 + 0.0005 = 12.0525 g.

The sensitiveness of a balance varies slightly with the load. It is simplest to determine once for all the sensitiveness for 50 g, 20 g, 10 g, 5 g, and 2 g, place a card in the balance with the results obtained, and use the numbers as required.

In this way the sensitiveness of a balance was found to be as shown below:

LOAD IN GRAMS	NUMBER OF SCALE DIVISIONS
50	2.23
20	2.28
10	2.64
5	2.66
2	2.66

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[1] As most analytical balances will scarcely detect with certainty less than 1/10 mg, the weight is expressed only to the fourth decimal. If the fifth decimal place in a calculation amounts to 5 or more, the number in the fourth decimal place is increased 1.

The determination of the zero reading, however, should be made with every weighing. If a number of weighings are to be made one after another it suffices to determine the zero point at the beginning and at the end and to use the mean of the two determinations. With very heavy loads, however, the zero reading should be determined before and after each weighing and the mean value used.

Balance-Arm Error

Both the preceding methods of weighing are subject to a constant error if the lengths of the balance arms are not exactly the same. Such an error can be corrected by the following methods of *indirect weighing.* The balance beam may be regarded as a lever with the fulcrum in the middle. In a lever, equilibrium results when the statical moments are equal. By *statical moment* is understood the product of the force and the length of the lever arm, and the length of the lever arm is the perpendicular distance from the axis of revolution (the fulcrum) to the line of action of the force.

Borda's Method of Weighing by Substitution

Place the object Q in the left pan and counterbalance or tare it by means of shot, sand, or weights. Then remove Q and establish equilibrium again by placing weights in its place. We have, then, as a result of the first weighing,

$$Ql = Tl_1$$

and from the second weighing,

$$Pl = Tl_1$$

from which it follows that:

$$Ql = Pl$$

$$Q = P$$

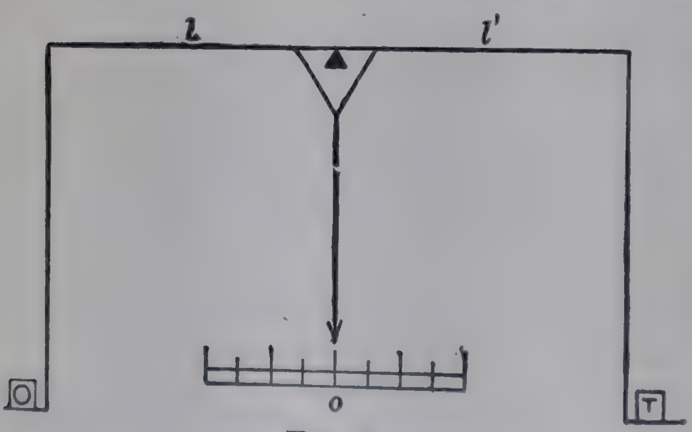

Fig. 3.

This method is used chiefly in weighing large objects.

Double Weighing

Place the object Q on the left pan and balance it against weights on the right pan. When equilibrium is reached

$$Ql = W_1l'$$

when W_1 represents the weights used, l the length of the left balance arm, and l' the length of the right arm. Transfer the object to the right balance pan and balance it with weights on the left pan. Then, if W_2 represents the necessary weights,

$$Ql' = W_2l$$

Multiplying the first equation by the second one we get

$$Q^2ll' = W_1W_2ll' \quad \text{or} \quad Q^2 = W_1W_2 \quad \text{and} \quad Q = \sqrt{W_1W_2}$$

If the balance is perfect, W_1 will be the same as W_2, and with any good balance the difference between the two values will be small; the algebraic mean then is practically the same as the geometric mean so that no sensible error is caused by assuming that the true weight is

$$\frac{W_1 + W_2}{2}$$

Reduction of Weighings to Vacuo

When a substance is immersed in water it experiences a buoyant or floating effect. Its true weight is diminished by the weight of water that it displaces. In exactly the same way, an object weighed in air against brass weights is buoyed up by the air that it displaces, but the weights are also subject to the same effect. If brass is weighed in air against brass weights, the buoyancy will be the same on both sides of the balance and the weight will be the same in a vacuum as in the air. If a material of lower density is weighed against brass, the weight in a vacuum will be greater than the apparent weight in air, and conversely, if a denser material such as gold is weighed with brass weights, the weight in a vacuum will be smaller than the weight in air.

The degree of precision attainable in the buoyancy correction depends upon the precision with which the volumes and the density of air can be determined. Several materials are used in the construction of every set of weights. The larger weights may be gold, gold-plated, or brass, and the smaller weights may be of platinum, German silver, or aluminum. Moreover, many brass weights have interior cavities with enclosed air. The chemist does not need to take these facts into consideration and can assume that all his weights are of solid brass, as will be explained later. The density of the air varies with the temperature, moisture and carbon dioxide content, barometric pressure, and the value of gravity. Since, however, in chemical work relatively small volumes of materials are used for the weighings, it is not necessary to consider slight variations in these factors.

Ordinarily, the weight of 1 ml of air at room temperature is assumed to be 1.2 mg,[1] and the density of brass weights is assumed to be 8.4.

If d_1 denotes the density of the object weighed, d_2 the density of the weights, ρ the weight of 1 ml of air, p_0 the weight in vacuo, and p the weight in air, the weight in vacuo can be found by the following formula:

$$p_0 = p + \left(\frac{p_0}{d_1} - \frac{p}{d_2}\right)\rho$$

If the density of air is assumed to be 0.0012, which is accurate to only two significant figures, and the density of the substance is given to only two significant figures, not more than three significant figures should be used in the value of p_0 and p in the parenthesis. In the parenthesis, therefore, p_0 can be replaced by p, and we have

$$p_0 = p + \left(\frac{p}{d_1} - \frac{p}{d_2}\right)\rho$$

The use of the above formula can be illustrated by a simple example. If a platinum crucible weighs 15.6954 g in the air with brass weights, what would the crucible weigh in a vacuum? In this case, $p = 15{,}6954$, $d_2 = 8.4$, and $d_1 = 21.4$. Substituting these values in the formula we have

$$p_0 = 15.6954 + \left(\frac{15.7}{21.4} - \frac{15.7}{8.4}\right)0.0012 = 15.6954 + (0.734 - 1.87)0.0012 = 15.6940$$

It would be a waste of time to try to get the value of the parenthesis with greater accuracy unless the density of the materials is known with greater precision than is assumed here. Note, however, that the value of ρ is usually given in milligrams but is used here in grams.

The student will naturally ask at this point why so much emphasis has been placed upon *brass* weights and why it is assumed that the weights are of brass even although they may be gold-plated or made of platinum. If a set of weights is sent to the Bureau of Standards for calibration and is to be used for very precise work, the Bureau will furnish a certificate which will have two series of corrections. One series will refer to the *apparent mass* as found by comparison with brass standards in air. The other series will make full allowance for the buoyant effect of the air and will refer to the *true mass* of each weight. Since the chemist does his weighing in the air he is interested only in the first set of corrections. With these corrections, the weight obtained in the air is that which would be obtained if the weights were of brass.

To make this point clear, it may be repeated that the larger weights may be gold-plated and some of the smaller weights may be of platinum and the smallest

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[1] The actual weight in milligrams of 1 ml of air varies with the temperature and pressure as the following table shows.

	16°	20°	22°	24°	26°	28°
730 mm.	1.17	1.15	1.14	1.13	1.12	1.11
750 mm.	1.20	1.18	1.17	1.16	1.15	1.14
770 mm.	1.23	1.21	1.20	1.19	1.19	1.18

may be of aluminum. The chemist wants his 10-mg weight to represent exactly $\frac{1}{100}$ of his gram weight when the weighing takes place without any allowance for the buoyant effect of air. This is accomplished by comparing the weights against brass standards in the air. In other words, the 10-mg weight although it may be made of aluminum will represent, when used in the air, exactly $\frac{1}{100}$ of a standard brass weight, but its true mass will be more than 10 mg.

Calibration of a Set of Weights[1]

A set of weights as furnished by the maker cannot as a rule be relied upon closer than to 0.5 mg for weighings of about 1 g. For exact work in absolute weighing it is necessary to determine not only the relative errors of the weights among themselves but also the absolute error of the set by comparing one of the largest pieces with a standard weight.

Weights are tested by the National Bureau of Standards upon application and the payment of a suitable fee. The Bureau of Standards recognizes six classes of weights. Class T are ordinary trade weights which are not tested by the Bureau except when there is no local authority to whom they can be submitted, or in the event of an important controversy. The laboratory weights used for rough weighings usually belong to this class. Class C weights are more accurate than those of Class T, and the permissible errors are only one-tenth as much. Classes A and B have allowable errors of about one-fifth as much as Class C, but the correction for each weight of Class A is determined accurately so that allowance for this error can be made in using the weight.

For the more precise weighings of the chemical laboratory, weights of Class S should be used. Class M weights are recommended for scientific work of the highest possible precision, but when the corrections for each member of a Class S set of weights is known, the set can be used with practically the same accuracy as a Class M set.

The analytical chemist rarely needs to know the absolute weight of anything. Almost all his work is expressed in percentages of an original weight taken. If every weight in the box were exactly twice as heavy as it is marked, the results of analysis would be the same, provided that such a set of weights were used exclusively, as if each weight were correct. The chemist, therefore, is much more interested in knowing the relation of the weights to one another than in knowing the actual error of any particular piece. A set of weights calibrated in terms of any weight of the set is satisfactory for the purposes of exact quantitative analysis.

Procedure. Mark the duplicate weights in the set so that they are distinguishable from one another. Thus a small dot can be made with a punch upon the second piece; if there are three pieces of the same denomination, the third can be given two punch marks. When the marking is properly done, no appreciable change in weight results.

If the beam of the balance is divided into five divisions and takes a 5- or 6-mg rider, start the calibration with the 5-mg weight. If the beam is divided into ten large divisions and carries a 10- or 12-mg rider (cf. p. 5), start with the 10-mg piece. Let us assume that the balance used is a short-arm Becker balance which takes a 6-mg rider and that the beam reads to about 5.5 mg on the scale.

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[1] It is well that each student should calibrate the set of weights furnished him. Many good teachers make this the first laboratory problem of a course in quantitative analysis. If the calibration of the weights is postponed to a later period, the student is likely to get more work done in the course.

Place the 5-mg piece whose value is to be tested on the left balance pan and another weight of the same denomination (borrowed from another set) on the right pan. By the method of swings (see p. 8), if an undamped balance is used, determine the rest point, r_1, when the balance is in equilibrium. Now transpose the two weights and determine the rest point r_2 with the weight to be tested on the right balance pan. It is convenient, with a balance in which the beam is graduated only on the right balance arm, to place a small permanent load (a piece of paper or of fine aluminum wire) on the left pan so that all the readings are near the middle of the balance arm. For the calibration assume temporarily that the borrowed weight is correct. In determining the values of r_1 and r_2, carry out the calculations to the nearest 0.05 of a scale division. The sensitivity of the balance should be at least three scale divisions (on the pointer scale) per milligram, and preferably 1 mg = about 5 divisions. From the values r_1 and r_2 the weight of the 5-mg piece tested is

$$5 - \frac{r_2 - r_1}{2S} \quad \text{mg}$$

where S = sensitivity of the balance (see p. 3).

Now take one of the 10-mg pieces, place it on the left balance pan, and weigh it against the two 5-mg pieces. Determine the values of r_1 and r_2 exactly as before. Always start with the pieces already tested on the right pan and the new weight on the left pan; unless the work is done methodically there is danger in getting the sign of the correction wrong. In fact, the commonest error in carrying out a calibration for the first time is to get this sign wrong. One must constantly bear in mind that the piece should have a negative correction if it is too light and a positive correction if it is too heavy. When the piece is too light, r_1 will be smaller than r_2.

Continue testing each weight in the set as follows:

$10^{\cdot}$ mg	against	10
$10^{\cdot\cdot}$	"	10
20 mg	"	$10 + 10^{\cdot}$
$20^{\cdot}$	"	20
50 mg	"	$10 + 10^{\cdot} + 10^{\cdot\cdot} + 20$ or against $20 + 20^{\cdot} + 10$
0.1 g	"	$0.05 + 0.02 + 0.02^{\cdot} + 0.01$
$0.1^{\cdot}$ g	"	0.1 g
0.2 g	"	$0.1 + 0.1^{\cdot}$ g; etc.

CALIBRATION OF WEIGHTS BY TRANSPOSITION

W_1 in Grams	W_2	r_1 in Scale Divisions	r_2 in Scale Divisions	S in Divisions per Milligram	$\frac{r_2 - r_1}{2S}$ Milligram	W_3	W_4	Correction in Milligrams
0.005	temporary standard	....	....	...	......	0.00500	0.00502	−0.02
0.005·	5 mg	4.7	4.4	4.5	−0.03	0.00503	0.00502	+0.01
0.010	5 + 5· mg	4.6	4.6	4.5	0.00	0.01003	0.01004	−0.01
0.020	10 + 5 + 5· mg	4.65	4.55	4.5	−0.01	0.02007	0.02007	−0.00
0.020·	20 mg	4.7	4.3	4.5	−0.05	0.02012	0.02007	+0.05
0.050	20 + 20· + 10 mg	4.3	4.9	4.5	0.07	0.05015	0.05018	−0.03
0.100	50 + 20 + 20· + 10 mg	5.0	4.8	4.0	−0.03	0.10034	0.10036	−0.02
0.200	100 + 50 + 20 + 20· + 10 mg	5.05	4.25	4.0	−0.10	0.20081	0.20071	+0.10
0.200·	200 mg	4.3	5.2	4.0	0.11	0.20070	0.20071	−0.01
0.500	200 + 200· + 100 mg	4.4	4.8	4.0	0.05	0.50180	0.50178	+0.02
1.000	500 + 200 + 200· + 100 mg	4.6	4.6	4.0	0.08	1.00365	1.00356	+0.09
2.000	1 g + 500 + 200 + 200 + 100 mg	3.9	5.4	4.0	0.19	2.00711	2.00712	−0.01
2.000·	2 g	4.4	4.8	4.0	0.05	2.00706	2.00712	−0.06
5.000	2 + 2· + 1 g	4.45	4.2	4.0	−0.03	5.01785	5.01781	+0.04
10.000	5 + 2 + 2· + 1 g	4.4	4.8	3.9	0.05	10.03562	10.03562	0.00
20.000	10 + 5 + 2 + 2· + 1 g	4.3	3.6	3.9	−0.09	20.07138	20.07124	+0.14
20.000·	20 g	4.7	2.2	3.5	−0.36	20.07174	20.07124	+0.50
50.000	20 + 20· + 10 g	3.45	3.0	2.7	−0.08	50.17882	50.17810	+0.72

Finally, when every piece in the set has been tested, arrange the data as shown in the table on p. 15. Under the heading W_1 is given the denomination of the weight which is first placed in the left balance pan. Under W_2 is given the temporary value of the weight or weights against which the new piece is tested. The values under r_1, r_2, S, and $\frac{r_2 - r_1}{2S}$ are obtained as described on p. 14. The values given under W_3 represent the temporary calibration values, which are based on the assumption that one of the smallest weights is correct, and those under W_4 are based on the assumption that one of the 10-g weights is correct. When this last assumption is made, it is easier to apply the corrections, as will be evident from the values under W_3 and the final corrections.

The calibration of weights is often done by weighing by substitution; another set of weights can be used conveniently as tares. Such weighing *by substitution* (p. 10) is a little easier to explain, but the corrections are more precise in the method of double weighing or weighing *by transposition.* Instead of assuming that one of the 10-g pieces is correct, some prefer to make a comparison with a standard weight, certified by the Bureau of Standards, but this is unnecessary.

Prepare a card from the individual corrections to show the corrections which should be applied to the usual combinations from 0.01 to 1.00 g and from 1 g upward, and keep this card in the balance case. In an ordinary gravimetric analysis, record the weights as follows:

	OBSERVED WEIGHT	CORRECTED MILLIGRAM	CORRECTED WEIGHT
Weight crucible + substance........	19.3105	+0.39 −0.01	19.3109
Weight crucible alone..............	16.9916	+ .06 + .06	16.9917
Weight of substance..............			2.3192

The upper correction is that of the weights of 1 g and over; the lower is that of the fractional weights.

When weights are tested at the National Bureau of Standards, each weight is called satisfactory if the error is not greater than a certain value which is called the *tolerance.* The following table shows the tolerance of Class S weights which are suitable for use in analytical chemistry and the precision to which the corrections are determined.

For practical purposes it is advisable to use weights of which the errors are not greater than the tolerances shown in the following table. Then, even if all the errors are of the same sign, no serious error is introduced in an analysis by using the uncorrected values because very few of our procedures have greater accuracy than 1 part in 1,000 and the values specified in the table are all more accurate than this except for the two smallest weights. The most satisfactory plan, therefore, is to make the weights correspond to the standard set by the table below. If a weight is a little too large, owing to corrosion, it can be burnished with fine emery cloth or with metal polish. A burnished weight should stand at least 10 minutes before a final test is made. If the weight is too small it should be rejected, unless it is a brass weight with a removable top, when a suitable piece of aluminum wire can be placed inside the piece. The use of lead for this purpose is unsatisfactory because lead corrodes too much.

PRECISION OF CORRECTION AND TOLERANCES OF WEIGHTS SUITABLE FOR QUANTITATIVE CHEMICAL ANALYSIS

Denomination	Precision	Tolerance	Denomination	Precision	Tolerance
100 g	0.5 mg	0.5 mg	500 mg	0.01 mg	0.05 mg
50	0.1	0.3	200	0.01	0.05
20	0.1	0.2	100	0.01	0.05
10	0.05	0.15	50	0.01	0.03
2	0.05	0.10	10	0.01	0.01
1	0.05	0.10	5	0.01	0.01

For testing weights to see whether they conform to the above standards, a balance sensitive to 0.05 mg and one set of calibrated weights is necessary. The calibration of weights is too tedious and involves too many calculations to make it a satisfactory experiment for beginners. Moreover, when a beginner calibrates a set of weights he is likely to make errors either in his computations or in applying the corrections. Often he will make a negative correction when it should be positive. Every set of weights should be tested at least once a year.

Weighing Samples of Factor Weights. In a busy laboratory it is often desirable to weigh out samples in such a way that the results of the analyses are known with as little computation as possible. Thus if the iron content of a sample weighing 0.6994 g is determined by weighing ferric oxide, Fe_2O_3, the percentage of iron, Fe, is exactly 100 times the weight of the oxide. If 1 ml of standard hydrochloric acid will neutralize 0.028 g of pure sodium carbonate, then the percentage purity of a sample of sodium carbonate, containing no other substance of basic nature, will be just twice the number of cubic centimeters of acid used in the analysis of samples weighing 1.4 g. In every technical laboratory, therefore, the chemist has to learn to weigh out rapidly samples of specified weights. If the sample is a dry powder, unaffected by contact with the air, it can be weighed out on a watch glass. It is convenient to have a pair of counterpoised watch glasses for this purpose, *i.e.*, a pair of watch glasses which weigh so nearly alike that they can be balanced with the aid of the rider. Metal pans weighing almost exactly 10.000 g can now be purchased and are convenient to use instead of watch glasses.

Place on the left balance pan the watch glass which is to hold the substance, and on the right pan place the tare of the watch glass and additional weights amounting to the desired quantity. With the aid of a small spatula, or a palette knife, transfer some of the powder to the watch glass in the left pan, until the pointer swings to the right with the beam lowered slightly so that the pointer can swing but a little way. Raise the beam, remove a little of the powder, and, with the beam again lowered a little, add more powder by tapping the spatula. By repeating this process once or twice and finally testing with the balance beam altogether lowered, it is possible to get any desired weight within 0.1 or 0.2 mg. In chemical work it is a waste of time to try to make the original weight much more accurate than the rest of the analysis. Thus, in determining the carbon content of a sample of steel with approximately 1 per cent of carbon present, the results of duplicate analyses with equal weight samples would be considered satisfactory if they indicated 1.00 and 1.01 per cent of carbon. In other words, errors arising from lack of homogeneity and inaccuracies in the method of analysis may easily amount to $\frac{1}{100}$ of the total carbon content. An error of 0.01 g in the weight of a gram sample of the steel would be no greater than the allowable error of the analysis. In weighing out the sample, therefore, if the weight is accurate to the nearest centigram the error is less than that of the remainder of the work. On the other hand, in determining the chlorine content of a sample of salt weighing about 0.25 g it is important to get the weight to the nearest tenth of a milligram because the chlorine determination can be accomplished with an accuracy of 1 part in 1,000 with samples of this size.

Reliability of a Result. In order that the result of any measurement may be of scientific or technical value, it is desirable to have some numerical estimate or measure of its validity. By the *accuracy* of a result should be understood the degree of concordance between it and the true value of the quantity measured. The true value is not usually known, so that it is not always possible to obtain a numerical measure of the absolute accuracy of a measurement or analysis. By the *precision* or *precision measure* of a result is understood the best numerical measure of its reliability after all known sources of error have been eliminated or allowed for.

When any quantity is measured to the full precision of which the instrument or method is capable, it will usually be found that the results of repeated measurements do not agree exactly. Thus in the analysis of pure salt, the chlorine content will not always be found to be exactly 60.66 per cent although we may have reason to believe that this is the correct value.

All that we can hope to obtain from experimental data is the most probable value of the quantity or quantities in question. The mathematical theory which treats of the general problem of the adjustment of errors of observation so that their effect upon the final result is reduced to a minimum is called the *method of least squares.* According to the theory, the most probable values of a series of related observations are those for which the sum of the squares of the errors is a minimum. This is not the place to go into the details of the mathematical proofs of the method of least squares, but it is important that every chemist should keep constantly in mind certain deductions that have been made from such studies.

In a series of observations, all of which possess an equal degree of probability, the most probable value of the quantity is the arithmetical mean. Since the true value of the quantity is not usually known, the error of each determination and of the mean cannot be determined. It is possible, however, to state how far each observation differs from the mean value, and from these differences the *probable deviation* of the mean can be estimated. The average deviation of the mean, usually designated as *ad*, is determined by dividing the sum of the deviations from the mean by the number of determinations made. The *ad* may be regarded as a numerical measure of the amount by which a new observation is likely to differ from the mean value, m.

Since the mean has a higher degree of probability than any single observation, it should have a smaller deviation from the truth. It can be shown that an arithmetical mean computed from n equally reliable observations is $\sqrt{n}$ times as reliable as any one observation. The deviation of the mean is usually denoted as AD. According to the statement just made,

$$AD = \frac{ad}{\sqrt{n}}$$

A little study of this expression shows that it does not pay to increase the number of observations beyond a certain limit as the time and labor involved soon become excessive.

It is probable that more than half the time spent on chemical and physical computations is wasted by the retention of more figures than the precision of the data warrants. The habit should be acquired of rejecting at each stage of the work all figures which have no influence on the final result. In the following rules for computation the term *digit* denotes any one of the ten numerals including the zero, and the term *significant figure* is any digit which denotes or signifies the amount of the quantity in the place in which it stands. Thus a zero may or may not be a significant figure. When it is used merely to locate the decimal point as in the values 1000 and 0.001, the zero is not a significant figure, for the position of the decimal point is determined solely by the unit in which the quantity is expressed. There are two significant figures in the value 2.5 mg even when it is written 0.0025 g. The number of decimal places in a result has in itself no significance in indicating the precision of a measurement. The statement that the results of an analysis agree within 1.2 mg gives no idea of the precision unless the entire value is known. A fractional or percentage precision measure, on the other hand, gives a definite idea of the precision of the measurement as it involves both the value of the quantity and its average deviation.

Rules for Computations

Rule I. In rejecting superfluous figures, increase by 1 the last figure retained if the following figure (that has been rejected) was 5 or over.

Rule II. In all deviation and precision measures retain two, and only two, significant figures.

Rule III. Retain as many figures in a mean result, and in data, as correspond to the second place of significant figures in the deviation or precision measure. According to this rule, two places of unreliable figures are retained in data so that accumulated errors due to rejections in the course of computation will not affect the first place of uncertain figures. Or, looked at from another point of view, the last figure may be regarded as quite unreliable but the next to the last significant figure should not vary by more than *one* or at the most *two* units from the mean.

Rule IV. The sum or difference of two or more quantities cannot be more precise than the quantity having the largest deviation. In adding or subtracting quantities, find the *ad* of each and retain in each quantity as many places as correspond to the second place of significant figures in the quantity with the largest deviation.

Rule V. In multiplication or division, the percentage precision of the product or quotient cannot be greater than the percentage precision of the least precise factor entering into the computation. Hence, determine the percentage precision of the least reliable factor. If this is about 10 per cent or better, use three significant figures in each factor of the computation and in the final result. If 1 per cent or better, use four significant figures in each factor of the computation and in the final result. If 0.1 per cent or better, retain five significant figures.

For computations involving a precision not greater than about 0.25 per cent use a 10-inch slide rule.

Rule VI. In carrying out the operations of multiplication and division by logarithms, retain as many places in the mantissa of the logarithm of each factor as are properly retained in the factors themselves under Rule V.

In ordinary chemical work the percentage precision of the result is often less than 0.1 per cent. Thus, in the determination of the chlorine content of a sample of pure salt weighing about 0.2 g, check values of 60.60 and 60.72 per cent chlorine would usually be considered satisfactory. This corresponds to a *percentage precision* of 0.12 part in 61.0, or 0.2 per cent. According to the above rules, only *four* figures should be retained in all factors entering into this computation, and four-place logarithms should be used. In the computation, the molecular weight of silver chloride should be taken as 143.3 instead of 143.34. If, on the other hand, a series of determinations all gave values ranging between 60.63 and 60.69 per cent chlorine, one would be justified in keeping *five* significant figures and using five-place logarithms. This would not necessarily mean that the original weight of the salt and the final weight of the precipitate would have to be carried out to five significant figures, because an error of 0.0002 g in about 0.2 g of salt would correspond to only 0.1 per cent of the entire weight. One would be justified, however, in recording the weights to five decimal places, using the method of swings.

For most chemical work, four significant figures are sufficient. In some cases, as in the determination of sulfur in steel, or in the conversion of small volumes of a solution (less than 1 ml) into an equivalent volume of some other solution, only two significant figures should be used.

HOME PROBLEMS

1. Find the weights in a vacuum of two crucibles, one of gold, *d* 19.3, and one of aluminum, *d* 2.7, each weighing 15.0000 g in air at 20° against brass weights.

2. A substance weighs 14.9654 g in air against brass weights and has a volume of 2ml. Find the weight in a vacuum.

3. With weights reduced to a vacuum basis, oxygen is 15.88 times as heavy as hydrogen. On a vacuum basis, the atomic weight of oxygen is 16 and that of hydrogen is 1.008. If 1 l of hydrogen weighs 0.0900 g in a vacuum, calculate the weight of

1 l of oxygen in the air with brass weights, and from this calculate the atomic weight of hydrogen in air, if oxygen is 15.995 in air.

4. If an analyst finds 55.12 per cent Fe when actually 55.41 per cent was present calculate the *absolute* and the *relative* percentage errors. *Hint.* The absolute error is calculated on the weight of sample, and the relative error on the actual percentage present.

5. In the analysis of a sample containing 41.65 per cent of a certain constituent, a student obtained the values 42.36, 42.25, and 42.48. Calculate the average deviation of the mean, *ad*, and the *AD*.

6. One gram is equivalent to 0.0352739 ounce, avoirdupois. What value should be used in converting 15.6 g into ounces?

7. If a sample contains 8.350 per cent of a certain constituent, what is the largest value which will show a relative error of 0.2 per cent (2 parts per 1,000)?

8. If the 5-g piece has the value 5.0118 when the 5-mg weight is the temporary standard, what is its value when a 10-g piece with temporary value 10.0236 is taken as standard?

CHAPTER II

VOLUMETRIC ANALYSIS. APPARATUS AND UNITS

The fact that silver chloride is practically insoluble in water furnishes the basis of qualitative tests for both silver and chlorine and for the quantitative determination of both these elements. There are two ways in which this can be done. Thus the weight of the silver chloride precipitate from a known weight of sample furnishes sufficient data for the computation of the percentage of chlorine present. Such an analysis is called *gravimetric* because the computation is based upon weights. The second way of carrying out the analysis is to measure the volume of silver nitrate solution required to precipitate completely all the chloride present. Then if the concentration of the silver nitrate solution is known, the chlorine content can be computed. This is called *volumetric* analysis because the result is obtained by measuring a volume. The process of determining the volume of reagent required to bring a definite reaction to completion is called titration. Many prefer, therefore, to call this *titrimetric analysis*. This term is less ambiguous because in gas analysis *volumes* are measured. For volumetric or titrimetric analysis, accurately calibrated measuring instruments are necessary.

Measuring Instruments

1. *Burets* are tubes of uniform bore throughout the entire length; they are graduated in milliliters[1] and are closed at the bottom, as shown in Fig. 4, by means of a glass stopcock, or with a piece of rubber tubing containing a glass bead *h*. The latter form was devised by Bunsen and is used as follows: Seize the tubing between the thumb and forefinger at the place where the glass bead is, and, by means of gentle pressure at the top of the bead, form a canal at one side of the bead through which the liquid will run out. Instead of the glass bead an ordinary pinchcock is sometimes used.

Besides the above forms of burets, many others are in use, but it is unnecessary to describe them here.

---

[1] The liter as defined by the National Bureau of Standards represents a volume of 1000.027 cubic centimeters. The one-thousandth part of a liter is called the milliliter, abbreviated ml. It is almost but not quite the same as a cubic centimeter, or cc.

2. *Pipets.* A distinction must be made between a *transfer* pipet and a *measuring* one. A transfer pipet has only one mark upon it, and serves for measuring off a definite amount of liquid. Transfer pipets are constructed in different forms; usually they consist of a glass tube with a cylindrical widening at the middle. The lower end is drawn out, leaving an opening about 0.5–1 mm wide. Pipets of this nature are constructed which will deliver respectively 1, 2, 5, 10, 20, 25, 50, 100, and 200 ml. For delivering these definite volumes of liquid, pipets are more accurate than burets or flasks.

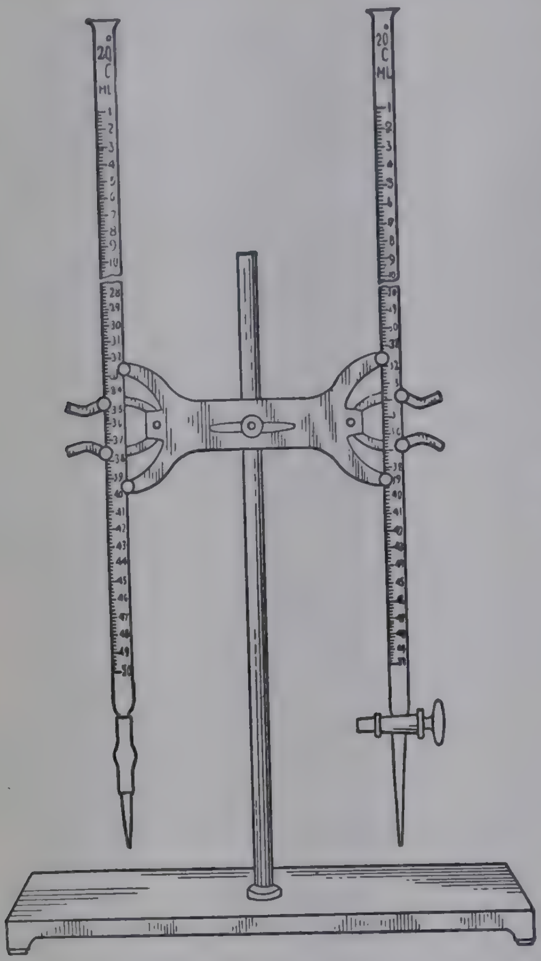

FIG. 4.

Measuring pipets are buret-shaped tubes graduated in milliliters and drawn out at the lower end. They serve to measure out any desired amount of liquid and are obtainable with a total capacity of 1, 2, 5, 10, 20, 25, and 50 ml.

3. *Measuring flasks* are flat-bottomed flasks with narrow necks provided with a mark, so that when they are filled to this point they will contain respectively 50, 100, 200, 250, 300, 500, 1000, and 2000 ml. They serve for the preparation of standard solutions and for the dilution of fluids to a definite volume.

4. *Measuring cylinders* are graduated in milliliters and are used only for rough measurements.

It is clear that accurate results can be obtained by a volumetric analysis only when the instruments used are accurately calibrated. It should never be taken for granted that a purchased instrument is correct, but it should always be tested carefully.

Normal Volume and Normal Temperature

A liter, which is the volume of a kilogram of water at its maximum density, is taken as the normal volume. If it is desired to mark on the neck of a liter flask the point to which this volume reaches, the position of the mark depends upon the temperature of the vessel. It is necessary, therefore, to choose for the vessel itself a definite temperature, the so-called *normal temperature.* At present the temperature of +20°C is taken as the normal temperature by the National Bureau of Standards. According to this, then, the flask should contain at 20° the volume that would be occupied by a kilogram of water at +4°, and as the kilogram is the unit of mass, the weighing should also take place in a vacuum.

The following table gives the density, or weight of 1 ml of water in a vacuum, at different temperatures.

DENSITY OF WATER AT DIFFERENT TEMPERATURES

t	Density	*t*	Density	*t*	Density
0°	0.999867	14°	0.999271	28°	0.996258
1	9926	15	9126	29	0.995969
2	9968	16	8969	30	5672
3	9992	17	8801	31	5366
4	1.000000	18	8621	32	5052
5	0.999992	19	8430	33	0.994728
6	9968	20	8229	34	4397
7	9929	21	8017	35	4058
8	9876	22	0.997795	36	0.993711
9	9808	23	7563	37	3356
10	9727	24	7321	38	0.992993
11	9632	25	7069	39	2622
12	9524	26	0.996808	40	0.992244
13	9404	27	6538		

It is experimentally impossible to weigh water at 4° in a glass vessel at 20° and in a vacuum, but with the aid of (1) the above table, (2) the known expansion of glass with rise in temperature, and (3) the buoyancies of water and of brass when surrounded by air, it is possible to calculate what the weight of 1 l of water is when weighed in the air at any temperature from 1° to 40°. The weights which must be placed upon the balance pan in order to determine the space occupied by a true liter of water, therefore, depend upon the temperature of the water and of the vessel, as well as the density of the air at the time of the experiment. The density of the air varies somewhat from day to day, depending upon the barometric pressure, the temperature, and the humidity. It usually suffices, however, to assume the average values of these factors, and in this way the following table has been computed to show the apparent weight in air with brass weights for temperatures between

15° and 30° under 50 per cent humidity and at a barometer reading of 760 mm.

If the glass vessel is at 20° no other correction is necessary. The glass, however, expands with rise of temperature. The coefficient of cubical expansion[1] varies from 0.000023 to 0.000028 per degree C. An average value of 0.000025 can be assumed.

APPARENT WEIGHT IN GRAMS OF WATER IN AIR

Temp. in Degrees C	2000 ml	1000 ml	500 ml	400 ml	300 ml	250 ml	150 ml
15	1996.11	998.05	499.03	399.22	299.42	249.52	149.71
16	1995.80	997.90	498.95	399.16	299.37	249.48	149.68
17	1995.48	997.74	498.87	399.10	299.32	249.43	149.66
18	1995.13	997.56	498.78	399.03	299.27	249.39	149.63
19	1994.76	997.38	498.69	398.95	299.21	249.34	149.61
20	1994.36	997.18	498.59	398.87	299.15	249.30	149.58
21	1993.95	996.97	498.49	398.79	299.09	249.24	149.55
22	1993.51	996.76	498.38	398.70	299.03	249.19	149.51
23	1993.06	996.53	498.26	398.61	298.96	249.13	149.48
24	1992.58	996.29	498.15	398.52	298.89	249.07	149.44
25	1992.09	996.04	498.02	398.42	298.81	249.01	149.41
26	1991.57	995.79	497.89	398.31	298.74	248.95	149.37
27	1991.04	995.52	497.76	398.21	298.66	248.88	149.33
28	1990.49	995.24	497.62	398.10	298.57	248.81	149.29
29	1989.92	994.96	497.48	397.98	298.49	248.74	149.24
30	1989.33	994.66	497.33	397.87	298.40	248.67	149.20

The expansion of water from 4° upward makes the weight of 1 liter of water smaller and, since water is less dense than the weights, weights of water in the air will always be less than they would be in a vacuum. If the temperature of the glass container is above 20°, the volume will be a little larger than it would be at 20°, which corresponds to greater weight, but this gain in weight is small compared with corrections caused by the expansion of water and by the buoyancy of the air so that, at the laboratory temperatures, the weight in grams is invariably a little smaller than the volume in milliliters. In the above table the weight in air of exactly the specified volumes of water is given. The table does not take into consideration the fact that the measuring vessel expands and if it reads correctly at 20° it will contain somewhat less at lower temperatures and somewhat more at higher temperatures.

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[1] At first sight it may seem strange to consider the cubical expansion of glass in calibrating. If, however, we consider a cube of glass with a cavity cut in it of 10-cm edge, then on heating it the cavity will expand to the same extent as if the glass had not been cut out. We measure, therefore, the cubic expansion of glass which has been removed in order to find the change in volume of a glass measuring vessel.

Thus a glass volumetric flask which holds exactly 1000.00 ml at 20° will hold 1000.25 ml at 30°, and this quantity of water will weigh 994.92 g in the air instead of 994.66 g as given in the table. The difference between the weight 994.92 and the volume 1000 ml is 5.08, and, when the flask is calibrated correctly within 1 ml of the specified volume, we can get the exact volume, within 0.01 ml, by adding the value 5.08 to the weight of the water when the temperature is 30°.

The following table is convenient for testing glass apparatus which is calibrated with the precision to be expected when purchased from reputable dealers. It gives values to add to the weight of the water in grams to get the number of milliliters which the glass measuring vessel indicates at 20°.

VOLUME OF ONE LITER FROM THE WEIGHT OF WATER IN AIR

Temp.	Add	Temp.	Add	Temp.	Add	Temp.	Add
15°	2.07	19.0	2.65	23.0	3.40	27.0	4.31
15.5	2.13	19.5	2.73	23.5	3.50	27.5	4.43
16.0	2.20	20.0	2.82	24.0	3.61	28.0	4.56
16.5	2.27	20.5	2.91	24.5	3.72	28.5	4.69
17.0	2.34	21.0	3.00	25.0	3.83	29.0	4.82
17.5	2.41	21.5	3.10	25.5	3.95	29.5	4.95
18.0	2.49	22.0	3.19	26.0	4.06	30.0	5.08
18.5	2.57	22.5	3.29	26.5	4.18		

This table can be used also for testing other volumes such as that of a 500-ml flask, a 100-ml flask, or a 50-ml pipet, when the proportionate fraction of the above values is taken. Thus in testing a buret by weighing 10-ml portions, add the above values in centigrams to the weight in grams, and the sum will show the volume in milliliters.

The above table is useful, but the student should know how to make the corrections without the table; the following example will show how this can be done.

Problem. Compute the volume at the standard temperature of 20° of a glass measuring flask from the following data:

Weight of flask filled to the mark with water at 24°	1136.40 g
Weight of the flask empty	140.58
Density of water at 24°	0.99732
Coefficient of cubical expansion of glass, per degree	0.000025
Density of weights, 8.4. Weight of 1 ml of air at 24° and 760 mm	0.00116 g

Reduction to Vacuum. Since the flask is weighed twice under the same conditions, it is unnecessary to correct its weight for the buoyancy due to air, but the observed weight of water, 1136.40 − 140.58 = 995.82 g, needs correction. In making the buoyancy correction only two significant figures are reliable here because the density of the weights was not given with greater accuracy. The volume of air displaced by the water is very nearly 1000 ml, and that of the air displaced by the weights is $1000 \div 8.4 = 120$ ml. The buoyancy correction is, therefore, the weight of 880 ml of air; $880 \times 0.00116 = 1.02$ g. The water in the flask would weigh $995.82 + 1.02 = 996.84$ g, if the weight could be made in a perfect vacuum.

Correction for Glass Expansion. The capacity of the flask increases from 20° to 24° to the same extent that glass would expand if it were present in the space occupied by the water, namely $1000 \times 0.000025 \times 4 = 0.10$ ml. Therefore, the volume will be 0.10 ml less at 20° than it is at 24°, and the weight of the water would be $996.84 - 0.10 = 996.74$ g; with this small volume of only two significant figures it is correct to say that 0.10 ml = 0.10 g.

Computation of the True Volume. Since the density of water at 24° is given as 0.99732 g, 1 l should weigh 997.32 g in a vacuum at 24° and a volume of 996.74 g corresponds to

$$\frac{996.74}{0.99732} = 999.42 \text{ ml}$$

This checks well with the value to be obtained by using the table on p. 27, according to which 3.61 g should be added to the apparent weight in air; $995.82 + 3.61 = 999.43$.

LABORATORY EXERCISES

Calibration of a Buret

A buret will not drain properly unless it is clean on the inside so that visible drops of liquid do not adhere to the sides when the liquid is withdrawn. "Cleaning solution," made from potassium dichromate and concentrated sulfuric acid, is efficient for cleaning burets and other glass apparatus. Dissolve 2 g of potassium dichromate in 5 ml of water, heating until all the salt has dissolved, cool the solution, and add slowly, while stirring, about 65 ml of concentrated sulfuric acid.[1] Considerable heat is evolved on the addition of the acid to the water. Fill the buret with the hot chromic acid solution, and allow it to stand 15 minutes or longer. Since this cleaning solution attacks rubber, it is best to remove the rubber tubing from the end of a Mohr or plain buret and force the end into a medium-sized cork stopper. Place a beaker under the buret while it is standing with the cleaning solution in it.

After 15 minutes, let the solution run out and rinse the buret at least four times with water. Then test to see if water drains freely without leaving drops adhering to the sides; if not, the cleaning process must be repeated. The cleaning solution can be kept and used repeatedly. It should be warm but not boiling hot when being used. Before pouring the used cleaning solution down the sink, remember to start the water running freely so that the acid will be largely diluted and will not attack the piping.

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[1] Cleaning solution containing 15 g $K_2Cr_2O_7$ or $Na_2Cr_2O_7$ in 500 ml of concentrated sulfuric acid is efficient for cleaning glassware. It should be kept in a glass-stoppered bottle and handled with care as it makes holes in clothing. If spilled it should be diluted with water and neutralized before being sponged up. Spilled concentrated acid should never be allowed to remain unneutralized on the floor or working bench.

Remove the stopcock of the glass-stoppered or Geissler buret, wipe it dry, and also wipe the inside of the ground joint in the buret. Smear the surface with stopcock lubricant,[1] and replace in the buret. Fasten the stopcock in place with some No. 24 copper wire.

Fill the buret with distilled water, making sure that the water extends to the very tip of the stopper with no air bubble there. To remove the air from a plain buret, raise the tip so that it is above the bottom of the buret and allow water to run out from the upturned tip; the lighter air tends to flow upward. The buret is now ready to be calibrated. Drain out water so that the upper level is close to the zero mark.

Weigh a 50-ml, flat-bottomed, narrow-necked flask to the nearest centigram. The outside of the flask must be dry, but it is not necessary to have the inside dry or cleaned with chromic acid solution. It is a waste of time to read the weight closer than to the nearest centigram, because one cannot read the buret closer than to the nearest 0.01 ml, and rapid weighing is advantageous to avoid error due to evaporation. Record the weight in the notebook. (See p. 30.)

Read the buret to the nearest 0.01 ml, and record the reading. Check each weight and each reading after setting them down in the notebook. In reading the buret, it is best to read the bottom of the meniscus, except with dark-colored liquids like potassium permanganate solution, in which case the top of the meniscus should be read. It is important that the eye should be directly opposite to the point read. If the eye is above the meniscus, the reading will be too high, and if the eye is too low the reading will be low. To avoid such parallax errors, the Bureau of Standards has asked the makers of burets to make the lines complete circles; the position of the eye is correct when the circle nearest to the bottom of the meniscus appears to be a straight line. When all the lines are circles, it is a little confusing to some eyes, so that some chemists prefer to use burets in which the lines of graduation do not extend very far and with lines of different lengths so that one can readily distinguish the whole and half milliliter lines. In such cases, it is well to take a strip of blue glazed paper with a straight and smooth edge. Wrap this strip around the buret evenly, with the colored edge on the inside. If the paper is placed about two divisions below the bottom of the meniscus, the eye will be level when the inside blue of the paper just comes into view. The blue also serves to make the tip of the meniscus appear a little darker and more sharply defined. With a little practice, one can easily learn to estimate the exact position of the meniscus within 0.01 ml.

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[1] Vaseline can be used as lubricant but is a little thin. *Lubriseal*, sold by the A. H. Thomas Co. of Philadelphia, is better. A good lubricant can be made by melting together, on the water bath, 16 parts of vaseline, 8 parts of pure gum rubber, and 1 part of paraffin.

After reading the buret, drain out 10 ml of water into the weighed flask stopping as closely as possible to the 10.00 mark but not wasting much time trying to get it exactly there because there will be a slight drainage while the weighing is being made.

Then, without stopping to make an exact reading of the buret, weigh the flask and its contents to the nearest centigram. After this read the buret and allow water to run into the flask until the 20.00 mark is reached, continuing in this way until the buret has been drained to the lowest calibration mark. Record the weighings in the notebook according to the following plan:

BURET CALIBRATION. TEMPERATURE 25°

Weights	Difference	Buret Readings	Difference	True Volume* of Each Portion	Correction for 10 ml	Total Correction
20.52		0.01				
30.50	9.98	9.96	9.95	10.02	+.07	+.07
40.52	10.02	19.95	9.99	10.06	+.07	+.14
50.47	9.95	29.93	9.98	9.99	+.01	+.15
60.39	9.92	39.91	9.98	9.96	−.02	+.13
70.40	10.01	49.85	9.94	10.05	+.11	+.24

When the calibration is finished, fill the buret again and repeat the work. In the second testing the corrections for each 10 ml should check with the first within 0.02 ml. From the average values, make a plot using one division of vertical distance on the paper to represent 1 ml of buret reading and each division of horizontal distance to represent 0.01 ml of correction. Then, on the plot, the total distance from the base line will show the correction to be applied for any given reading of the buret. Many burets are obtained today which are calibrated so accurately that there is no need for applying buret corrections, particularly if one always makes a practice of beginning at about the zero mark with every standardization and in every analysis. It is not safe, however, to assume that a buret is correct without testing it.

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* The table on p. 27 shows that the correction to be added to the weight of 1 l of water when weighed in the air at 25° is 3.83 g. For 10 ml ($\frac{1}{100}$ liter) the correction will be 0.0383 g. Since the buret cannot be read to less than 0.01 ml, the correction used is 0.04 g. For very accurate work, weight burets are used in which the stoppered buret is weighed at the start and finish of each analysis. With such a buret the analysis can be made more accurately; see p. 78.

Instead of calibrating the buret in the manner just described, many chemists prefer to start each time at the zero point, refilling the buret after each withdrawal of 10, 20, 30, or 40 ml of liquid. Others prefer to calibrate by causing the water to flow through a carefully calibrated small pipet, reading the buret after each withdrawal of a pipetful of water.

Calibration of a Pipet

Clean the pipet with cleaning solution, but take care not to suck any of the chromic acid into the mouth. To avoid this, attach a piece of rubber tubing to the pipet and apply suction through this tubing. Rinse out the pipet with water. Suck up distilled water to a point above the graduation mark, quickly place the forefinger over the top of the tube, and allow the level of the water to fall until the bottom of the meniscus coincides with the graduation mark. Then allow the contents of the pipet to run into a weighed flask; hold the pipet in a vertical position all the time. As soon as the pipet is empty, touch the tip to the inside surface of the flask and withdraw it. Do not wait for another drop to form and do not blow into the pipet. From the weight of the water, determine the volume of the pipet as in the calibration of a buret.

Calibration of a Flask

Flasks are sometimes calibrated both for content and for delivery. To test the calibration for delivery, clean and weigh the delivered water exactly the same as for burets and pipets.

To test the calibration for content. Clean carefully and dry the flask both inside and outside. Allow it to come to room temperature and weigh the empty flask. Then fill with water up to the mark and weigh again.

To calibrate an unmarked flask, preferably one having a narrow neck, clean, dry, and weigh (or tare[1] carefully). Then place the proper weight on the balance pan and add water until equilibrium is again restored. Note the place on the neck where the bottom of the meniscus comes.

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[1] The word *tare* is used to represent a counterpoise which may or may not be weights. If weights are used, it is not necessary to record the values.

Place the flask upon a level surface and fasten a piece of gummed paper with a straight edge around the neck of the flask so that its upper edge is just tangent to the deepest point of the water meniscus. Empty the flask, dry, cover its neck with a uniform layer of beeswax, and allow to cool; this usually requires about 15 minutes. Then hold the flask, as is shown in Fig. 5, against the piece of wood *s*, place the blade of a pocket knife firmly against the upper edge of the thick paper ring, and revolve the flask through 360° around its horizontal axis; in this way a circle is cut in the wax layer. By means of a feather place a drop of hydrofluoric acid[1] along this circle while holding the flask in the horizontal position. By turning the flask around its axis, allow the drop of hydrofluoric acid to act upon the glass where the wax coating has been cut. After 2 minutes wash the excess of hydrofluoric acid off, dry the neck of the flask by means of filter paper, heat until the wax melts, and wipe it off. Remove the last traces of wax by rubbing with a cloth wet with alcohol.

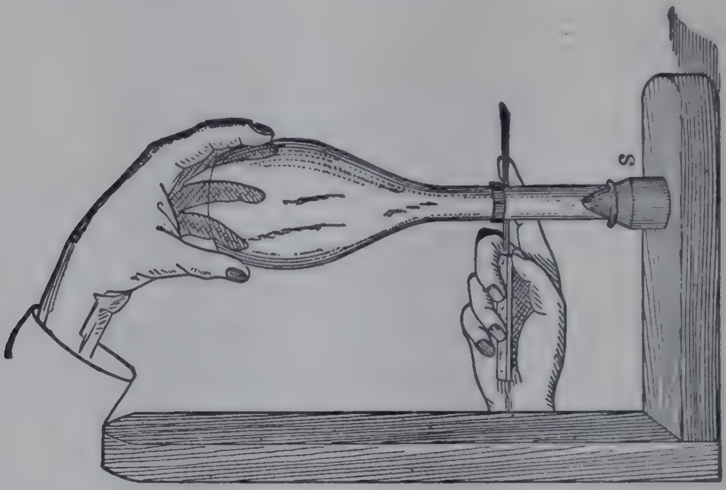

FIG. 5.

HOME PROBLEMS

9. Calculate to the nearest centigram the weight of water, as determined in air with brass weights, required to fill a 250-ml flask at 25° and 750 mm pressure, if the volume of the flask is exactly correct at 20°.

10. In testing the capacity of a 50-ml pipet, it was found to deliver 49.85 g of water. Find the capacity of the pipet assuming that gold weights were used (*d* 19.3), that 1 ml of air weighed 1.2 mg under the conditions of the experiment, and that the temperature of the water and laboratory was 17.5°.

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[1] Hydrofluoric acid produces painful burns. If any of the acid gets on the fingers, wash them well with water *at once.* The acid does not smart, or sting, at first because it has anesthetic properties.

11. In testing a buret with water at 23°, the following results were obtained:

Buret readings..........	0.02	10.12	20.09	30.16	40.19	50.00
Weights...............	16.27	26.35	36.26	46.34	56.31	66.17

From these data compute the buret corrections, using the data given on p. 27.

12. If the water in a volumetric flask weighs 398.16 g in the air at 28° find the volume of the water to the nearest 0.02 ml and the volume at 20° when the flask is filled with water to exactly the same place.

13. If 1.000 g of water (weighed in the air) has a volume of 1.003 ml at a certain temperature, find the density (weight of 1.000 ml in a vacuum) of the water at that temperature.

14. Make a sketch to illustrate the effect of parallax error when the eye is not on a level with the bottom of the meniscus in making a buret reading.

CHAPTER III

CONCENTRATION OF SOLUTIONS. CALCULATIONS OF VOLUMETRIC ANALYSIS

Volumetric analysis is based upon the measurement of volumes, but it is necessary to know the strength of the reagent used to accomplish a given reaction. The strength of a solution is determined by its *concentration* or the quantity of reagent in a given volume. A solution of silver nitrate reagent may be prepared by dissolving 25 g of solid silver nitrate in water and diluting the solution to 1 l. The concentration of the well-mixed solution can be expressed by saying that it contains 25 g of silver nitrate per liter, or 25 mg per ml. This method of expressing concentrations in *weight per unit volume* is a very common one. Sometimes the concentration is expressed in weight of solvent per unit weight of solute. Thus, the silver nitrate solution just referred to will contain 25 g silver nitrate in 997.2 g of water at 20°.

The chemist often speaks of a 10 per cent solution or a 20 per cent solution, etc. This is, as a rule, a rather careless way of expressing concentrations because the chemist usually means by a 10 per cent solution, as Wilhelm Ostwald pointed out, one that contains 10 g of reagent in 100 ml of solution. This method of expressing concentrations is used for approximate work when it does not make much difference whether the solution contains an exactly known weight.

In expressing the concentration of aqueous solutions of gaseous substances such as NH_3 or HCl it is common practice to say that the solution contains a certain *percentage by weight.* Thus the table at the back of the book shows that hydrochloric acid of 1.2 density contains 39.11 per cent HCl by weight. This means that 1 ml of the HCl solution weighs 1.2 g and contains 1.2×0.3911 g of dissolved HCl. In this particular case, the table gives the values on a vacuum basis.

Sometimes mixtures of two liquids are said to contain a certain *percentage by volume* of one of them. Thus, if 25 ml of pure alcohol is diluted with water to make 100 ml of solution, the mixture can be said to contain 25 per cent of alcohol by volume.

The physical chemist usually finds it convenient to express concentrations in *moles per liter*, the designation *mole* (German *mol*) meaning a molecular weight in grams. A solution containing 36.46 g of HCl per liter is called, therefore, a *molar* solution.[1] This designation is also applied to ions in solution; a solution is said to be molar in hydrogen ions if it contains 1.008 g of H^+ per liter.

Sometimes the molecular weight of a substance may be in doubt. Thus one chemist may write the formula of mercurous chloride as HgCl and another chemist may prefer Hg_2Cl_2. To avoid misunderstanding of this nature, some chemists make use of the term *formal solution* to represent one formula weight in grams per liter and give the formula of the substance.

There are other ways in which concentrations can be expressed using other units of mass and of volume. Thus the mass can be expressed in grains, ounces, pounds, or tons and the volume in pints, quarts, gallons, or cubic feet.

For the purposes of volumetric analysis none of the above methods of expressing concentration is entirely satisfactory. If we say that 1 ml of HCl solution contains 0.4693 g of dissolved HCl, it is a rather difficult problem in mental arithmetic to decide exactly how much NaOH it will neutralize. It involves the knowledge of the molecular weights of HCl, (36.46) and NaOH (40.01). We can carry out such a computation and find, for example, that 1 ml of the HCl solution will neutralize $0.4693 \times 40.01 \div 36.46 = 0.5151$ g of NaOH. This value expresses the concentration of the acid solution in terms of NaOH and is helpful if the acid is to be used for the sole purpose of analyzing samples of NaOH. Another computation is necessary to find out the strength of the solution with respect to any other substance with which it will react.

The most convenient method, however, of expressing the concentrations of solutions for the purposes of volumetric analysis is with reference to equivalent weights.

Normal Solutions

By a *normal solution* is understood one which contains *1 gram equivalent* of the active reagent dissolved in 1 l of solution.[2] By *gram equivalent* is meant the amount of substance equivalent to 1 gram atom (1.008 g) of hydrogen. One milliliter of a normal solution contains one *milli-equivalent* of active reagent. For convenience in computation the concentrations of solutions used for volumetric purposes are expressed in terms of their normality; that is, a solution is 2 normal, 0.5 normal, 0.1 normal, etc. The letter *N* is used as an abbreviation for *normal.*

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[1] A solution containing one mole in 1000 g of solvent is often called a *molal* solution. This distinction between a *molar* and a *molal* solution is emphasized by some and disregarded by other chemists.

[2] It is important to note that a normal solution is not properly defined as one containing a gram equivalent in 1 l of *solvent*. In volumetric analysis the unit is always referred to the volume of the solution. The *gram equivalent* will often be referred to as the *equivalent weight* of a substance. The equivalent weight will always refer to 1 l of solution and the milliequivalent to 1 ml.

The gram equivalent, or weight required to make a liter of normal solution, depends upon the nature of the reaction involved. It often happens that the same solution has a certain normal concentration when used for one purpose and a different normal concentration when used for another purpose. The reagents used in volumetric analysis are acids, bases, oxidizing agents, reducing agents, and precipitants.

The equivalent weight of an acid is determined by the number of replaceable hydrogen atoms in the acid molecule. Thus, to make a normal solution of the monobasic hydrochloric, hydrobromic, hydriodic, nitric, or acetic acids, it is necessary to have a molecular weight in grams (*1 mole*) of the acid dissolved in a liter of solution. To make 1 liter of normal solution of the dibasic sulfuric acid only ½ mole of the acid is necessary.

Sometimes, however, it is not convenient to react with all the replaceable hydrogen atoms of an acid. In fact some acids are so weak that they cannot be used in volumetric analysis. Carbonic acid, for example, has no appreciable effect upon methyl orange, and only 1 of the 2 hydrogen atoms in H_2CO_3 is acid toward phenolphthalein.

Phosphoric acid, H_3PO_4, really has 3 replaceable hydrogens, but only the first is acid toward methyl orange and 2 hydrogen atoms are acid toward phenolphthalein. In titrating with methyl orange as indicator, phosphoric acid acts as a monobasic acid and the normal solution contains 1 mole per liter. With phenolphthalein as indicator, phosphoric acid acts as a dibasic acid and ½ mole per liter will make a normal solution of phosphoric acid.

A normal solution of a base will contain 1 mole of replaceable hydroxide per liter. Thus of potassium hydroxide, KOH, sodium hydroxide, NaOH, and ammonium hydroxide, NH_4OH, 1 mole per liter makes a normal solution. Of barium hydroxide, $Ba(OH_2)$, calcium hydroxide, $Ca(OH)_2$, and strontium hydroxide, $Sr(OH)_2$, only ½ mole per liter is required. Magnesium hydroxide is not appreciably soluble in water, but it is convenient to use the conception of normal solution to determine how much will be dissolved by an acid solution of known strength. One liter of normal hydrochloric acid will dissolve ½ mole of $Mg(OH)_2$.

Salts of weak acids and strong bases have an alkaline reaction. With methyl orange as indicator, 1 mole of sodium carbonate reacts with 2 moles of hydrochloric acid; hence, the equivalent weight is ½ mole of sodium carbonate. With phenolphthalein, however, the end point is reached when 1 mole of sodium carbonate has reacted with 1 mole of hydrochloric acid; in this case the normal solution will contain 1 mole of sodium carbonate per liter. One molecule of borax, $Na_2B_4O_7$, reacts with 2 molecules of hydrochloric acid when methyl orange is the indicator. If after this neutralization considerable glycerol, $C_3H_5(OH)_3$, or some mannitol, $C_6H_8(OH)_6$, is added, one molecule of sodium hydroxide is required for each atom of boron in order to make the solution neutral to phenolphthalein.

The equivalent weight of an oxidizing agent is determined by the change in polarity which the reduced element experiences. The polarity of an element is the sum of the positive and negative valence bonds which it has in a compound; it represents the state of oxidation. Usually the polarity is the same as the valence except that a positive or negative sign is prefixed, but sometimes, as is true of the nitrogen atom of an ammonium salt, there is a difference. Nitrogen in the ammonium radical has a valence of 5, but four of the bonds are negative toward hydrogen atoms and the fifth bond is positive toward the acid ion of the ammonium salt. The polarity of nitrogen in an ammonium salt is -3 and it corresponds to the same state of oxidation as ammonia, NH_3.

When potassium permanganate is used as an oxidizing agent, the manganese drops to a lower polarity. In permanganate the polarity of the manganese atom is $+7$, and, in most reactions used in volumetric analysis, the manganese is reduced to manganous salt in which the manganese has a polarity of $+2$:

$$MnO_4^- + 5Fe^{++} + 8H^+ \rightarrow Mn^{++} + 5Fe^{+++} + 4H_2O$$
$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{++} + 5I_2 + 8H_2O$$

A normal solution of potassium permanganate, therefore, will contain ⅕ mole of $KMnO_4$ because the atom of manganese loses 5 positive charges in changing from a polarity of $+7$ to $+2$.

Sometimes, however, the manganese of potassium permanganate is reduced only to the quadrivalent state. Thus a hot, nearly neutral solution of a manganous salt can be made to react with permanganate as follows:

$$2MnO_4^- + 3Mn^{++} + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

In this case the manganese atom in permanganate loses only 3 charges and, strictly speaking, a normal solution of permanganate should contain only ⅓ mole of the reagent, but permanganate is usually standardized by a reaction in which it is reduced to manganous salt. *Throughout this book, therefore, a normal solution of permanganate will refer to one containing ⅕ mole of $KMnO_4$ per liter, and $2MnO_4^-$ will be regarded as 10 equivalents.*

Potassium dichromate is often used as an oxidizing agent. In it each chromium atom has a polarity of +6, and by reduction 2 trivalent chromic ions are formed. There is a loss in polarity of 3 charges for each chromium atom, and a normal solution of potassium dichromate, $K_2Cr_2O_7$, will contain ⅙ mole.[1]

$$Cr_2O_7^{=} + 6Fe^{++} + 14H^+ \rightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O$$
$$Cr_2O_7^{=} + 6I^- + 14H^+ \rightarrow 2Cr^{+++} + 3I_2 + 7H_2O$$
$$Cr_2O_7^{=} + 3Sn^{++} + 14H^+ \rightarrow 2Cr^{+++} + 3Sn^{++++} + 7H_2O$$
$$Cr_2O_7^{=} + 3H_2S + 8H^+ \rightarrow 2Cr^{+++} + 3S + 7H_2O$$

A solution of a ferric salt is sometimes used as a mild oxidizing agent. Thus, it will oxidize the iodide anion

$$2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$$

In this case, the oxidation depends upon the reduction of the ferric ion to the ferrous condition, and the equivalent weight of a ferric salt is the molecular weight divided by the number of Fe atoms in the molecule of the ferric salt.

Solutions of ceric salts have been highly recommended for replacing potassium dichromate and potassium permanganate in titrations. The oxidizing effect of the quadrivalent cerium cation depends on the reduction of the cerium to the trivalent condition. The ceric cation, Ce^{++++}, is reduced to Ce^{+++} about as easily as MnO_4^- is reduced to Mn^{++}. Ceric solutions are more stable than permanganate solutions, but the end point in a titration is not so easy to find. Usually it is best to determine the end point potentiometrically or with the aid of a colored substance that changes color when oxidized, such as diphenylamine or diphenylamine sulfonic acid.

$$Ce^{++++} + Fe^{++} = Ce^{+++} + Fe^{+++}$$

It is quite likely that the Ce^{++++} is present in a complex rather than as a simple ion.

The equivalent weight of a reducing agent is determined in like manner by the gain in polarity which the oxidized element experiences.

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[1] The valence of an ion containing more than one element is the algebraic sum of the polarities of its constituents. Except in peroxides, oxygen has a polarity of −2 in its compounds. The polarity of the chromium can be determined from the charge of the ion and that of the oxygen. The same is true of the permanganate ion or of any other complex ion. Thus, in $Cr_2O_7^{--}$ the chromium must have a polarity of +6 if each atom of oxygen has a polarity of −2, in order to get a charge of −2 on the $Cr_2O_7^{--}$.

Ferrous salts are oxidized to ferric salts, and the iron is changed from +2 to +3 in polarity. A normal solution of ferrous sulfate, $FeSO_4 \cdot 7H_2O$, or of ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, will contain 1 mole of either salt per liter.

As precipitants, the normal solutions are referred to the simplest type of salt in which each constituent has a valence of 1. Thus, of sodium chloride, $NaCl$, and of silver nitrate, $AgNO_3$, a normal solution will contain 1 mole per liter. Of sodium sulfate, Na_2SO_4, barium chloride, $BaCl_2$, and magnesium sulfate, $MgSO_4$, a normal solution will contain ½ mole per liter.

If potassium dichromate is used as a precipitant in the following reaction

$$Cr_2O_7^{=} + 2Ba^{++} + 2C_2H_3O_2^{-} + H_2O \rightarrow \mathbf{2BaCrO_4} + 2HC_2H_3O_2$$

the normal solution will contain ¼ mole per liter.

Oxalic acid and the acid oxalates are used sometimes as acids and sometimes as reducing agents. Oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, has 2 replaceable hydrogens when titrated against alkali with phenolphthalein as indicator, and its normal solution as an acid contains ½ mole per liter:

$$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$$

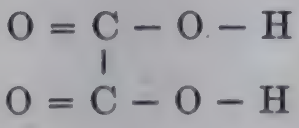
or

$$2H^{+} + 2OH^{-} \rightarrow 2H_2O$$

Oxalic acid also reacts with permanganate in accordance with the following equation:

$$5C_2O_4^{=} + 2MnO_4^{-} + 16H^{+} \rightarrow 2Mn^{++} + 8H_2O + 10CO_2$$

From the fact that the normal solution of permanganate contains ⅕ mole per liter, it is clear that the equivalent weight of oxalic acid as a reducing agent is ½ mole, just as when acting as an acid. In this case, however, the reducing power has nothing whatever to do with the hydrogen-ion content of oxalic acid, for the above reaction takes place in the presence of a mineral acid. The valence of carbon in oxalic acid is 4, and the structural symbol, leaving out the water of crystallization, is written thus:



$$\begin{array}{c} O = C - O - H \\ | \\ O = C - O - H \end{array}$$

This structural symbol shows that 3 valence bonds of each carbon atom are positive toward 2 atoms of oxygen but one bond of each carbon atom is neutralized by a valence bond of the other carbon atom. The effective valence of each carbon atom is therefore +3 toward O or OH. It becomes +4 when oxidized to CO_2. When oxalic acid is heated alone, H_2O, CO, and CO_2 are formed, and thus, without oxidation, bivalent and quadrivalent carbon atoms appear which correspond to the above assumption of an average polarity of +3.

The fact that the equivalent of $C_2O_4^{--}$ is ½ mole is also shown by the fact that the oxidation can be expressed by the equation

$$C_2O_4^{--} - 2e = 2CO_2$$

in which e represents the unit charge of the electron.

Potassium acid oxalate, KHC_2O_4, can be used as an acid

$$KHC_2O_4 + KOH \rightarrow K_2C_2O_4 + H_2O$$

in which case the equivalent weight is 1 mole of KHC_2O_4, but as a reducing agent the reducing power is due to the oxalate anion and a normal solution will contain only ½ mole of KHC_2O_4. A solution of KHC_2O_4 which is normal as an acid will be 2 N as a reducing agent.

Potassium tetroxalate behaves similarly. As an acid it has 3 replaceable hydrogens and the equivalent weight is ⅓ mole:

$$KHC_2O_4{\cdot}H_2C_2O_4{\cdot}2H_2O + 3NaOH \rightarrow KNaC_2O_4 + Na_2C_2O_4 + 5H_2O$$

As a reducing agent, potassium tetroxalate has two $C_2O_4^{=}$ groups and the equivalent weight is ¼ mole. If a solution of potassium tetroxalate contains 1 mole per liter, it is 3 N as an acid and 4 N as a reducing agent, and the same relation holds at all concentrations.

Preparation of Normal Solutions

The required amount of substance should be dissolved in water and diluted to a volume of 1 l at 20°. Often, however, the water is not at the normal temperature, so that it is customary to dissolve the substance in water at the laboratory temperature and then dilute the solution up to the mark in a liter flask. After the solution is thoroughly mixed its temperature is taken by a sensitive thermometer. If the temperature is above 20°, the volume of the solution would be less than 1 l if it were cooled to exactly 20°, so that the solution as made up is a little too strong. The following table shows how to correct for the temperature effect:

TEMPERATURE CORRECTION FOR VOLUMETRIC SOLUTIONS

Temp. of Measurement, °C	Capacity of Apparatus in Milliliters at 20°C						
	2000	1000	500	400	300	250	150
	Correction in Milliliters to Give Volume of Water at 20°C						
15	+1.54	+0.77	+0.38	+0.31	+0.23	+0.19	+0.12
16	+1.28	+0.64	+0.32	+0.26	+0.19	+0.16	+0.10
17	+0.99	+0.50	+0.25	+0.20	+0.15	+0.12	+0.07
18	+0.68	+0.34	+0.17	+0.14	+0.10	+0.08	+0.05
19	+0.35	+0.18	+0.09	+0.07	+0.05	+0.04	+0.03
21	−0.37	−0.18	−0.09	−0.07	−0.06	−0.05	−0.03
22	−0.77	−0.38	−0.19	−0.15	−0.12	−0.10	−0.06
23	−1.18	−0.59	−0.30	−0.24	−0.18	−0.15	−0.09
24	−1.61	−0.81	−0.40	−0.32	−0.24	−0.20	−0.12
25	−2.07	−1.03	−0.52	−0.41	−0.31	−0.26	−0.15
26	−2.54	−1.27	−0.64	−0.51	−0.38	−0.32	−0.19
27	−3.03	−1.52	−0.76	−0.51	−0.46	−0.38	−0.23
28	−3.55	−1.77	−0.89	−0.71	−0.53	−0.44	−0.27
29	−4.08	−2.04	−1.02	−0.82	−0.61	−0.51	−0.31
30	−4.62	−2.31	−1.16	−0.92	−0.69	−0.58	−0.35

[This table shows the correction to various observed volumes of water, measured at the designated temperatures, to give the volume at the standard temperature, 20°C. Conversely, by subtracting the corrections from the volume desired at 20°C, the volume that must be measured out at the designated temperature in order to give the desired volume at 20°C will be obtained. It is assumed that the volumes are measured in glass apparatus having a coefficient of cubical expansion of 0.000025 per degree centigrade. The table is applicable to dilute aqueous solutions having the same coefficient of expansion as water.]

For the following standard solutions more accurate results will be obtained if the numerical values of the above corrections are increased by the percentages given below:

Solution	Normality		
	N	0.5 *N*	0.1 *N*
HNO_3	50	25	6
H_2SO_4	45	25	5
NaOH	40	25	5
KOH	40	20	4
HCl	25	15	3
$H_2C_2O_4$	30	15	3
Na_2CO_3	40	25	5

Standardization of Solutions

If the reagent to be used in a volumetric analysis is known to be pure, it is best to prepare the standard solution as outlined on p. 40. Frequently, however, it is better to determine the concentration by testing the strength of the solution against some other substance known to be pure. Thus the strength of an acid solution can be determined by weighing out some carefully purified sodium carbonate and determining exactly how much of the acid solution is required to neutralize this weight of pure sodium carbonate. In this case the acid solution is said to be *standardized against* sodium carbonate and sodium carbonate is called the *standard* substance. Evidently, if the acid is a *normal* solution, each milliliter of solution will neutralize exactly 1 milliequivalent of the standard. The normal solution not only contains 1 milliequivalent of the active reagent in 1 ml but also it will react with 1 milliequivalent of other substances. In any standardization, therefore, if g is the weight of standard taken, ml is the number of milliliters of solution required to react with this weight of standard, and e is the milliequivalent weight of the standard used,[1] then the *normality* of the solution (or the number of milliequivalents in 1 ml) is $\frac{g}{ml \times e} = N$. Usually this is sufficient because the weight of substance that reacts with 1 ml of the standardized solution can be found by multiplying the milliequivalent weight of the substance analyzed by the value N. Sometimes, however, it is better to make the solution exactly normal, half-normal, or tenth-normal. To do this it is best to prepare the solution a little stronger than desired and then dilute it with water until the desired concentration is obtained. Then, if N is the normal concentration originally obtained, N' is the desired normality, V is the original volume taken, and V' is the volume after dilution, $N \times V = N' \times V'$ and $V' = (N \times V)/N'$. $V' - V$ is then the volume of water to be added to the volume V.

In volumetric work it is often desirable to have two solutions of reagents, one having the opposite effect to the other. Thus, in working with an acid, sometimes too much is added and it is convenient to have a standardized solution of a base at hand to neutralize the excess acid. It is not necessary to standardize the second solution independently, but it is important to know the relative strengths of the two solutions.

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[1] On p. 40, e was used to represent a unit of electricity, namely, a unit charge of 96,500 coulombs on a gram equivalent or $96{,}500 \div (6.06 \times 10^{23})$ coulombs on the actual atom or radical. Throughout the book, the italic letter e will be used in both ways, but this should not cause confusion.

If a ml of solution A are equal in strength to b ml of solution B, then 1 ml of $A = b/a$ ml of B and 1 ml of $B = a/b$ ml of A. If solution A is N-normal, then solution B is $(a \times N)/b$ normal. If, on the other hand, the solution A is known to be N-normal and solution B is known to be M-normal, then the relative strengths are: 1 ml of solution $A = N/M$ ml of solution B; 1 ml of solution $B = M/N$ ml of solution A.

General Method of Computing Results

Let *ml* represent the volume in milliliters of N-normal solution required to react with s grams of a substance of which the milliequivalent weight is e; then

$$\frac{ml \times N \times e \times 100}{s} = \text{per cent}$$

In the analysis of sodium carbonate, molecular weight 106.0, completely neutralized by hydrochloric acid, the value of e is 0.0530 and the result obtained by the above formula will be the percentage of Na_2CO_3 in the sample analyzed. If it is desired to express the result in terms of Na_2O, molecular weigh 62.0, the value of e is 0.0310. Or it may be desired to find the percentage of CO_2 in the sample on the assumption that nothing else but Na_2CO_3 is present that will react with the acid used. In this case the value of e is 0.022. In using the above formula, therefore, it is necessary to bear in mind that the value of the milliequivalent should be in terms of the substance desired. The value $N \times e$ is called the *titer* of the solution with respect to the substance of which e is the milliequivalent weight. Thus e for Na_2O is 0.0310 g, and for 0.5 N HCl the titer in terms of Na_2O is $0.5 \times 0.031 = 0.0155$ g Na_2O, which means that 1 ml of 0.5 N HCl will neutralize 0.155 g Na_2O.

Sometimes, it is desirable to avoid computations in technical work and it is convenient to weigh out a sample such that the buret reading will give the percentage desired (cf. p. 17). This will be always true if the weight of sample is $100 \times N \times e$, as inspection of the above equation will show. Or, if the weight of sample is $50 \times N \times e$, then the desired percentage will be found by multiplying the *ml* used by 2.

HOME PROBLEMS

15. How many grams of each of the following substances are required for 1 l of normal solution: KOH, H_2SO_4, HCl, $H_2C_2O_4 \cdot 2H_2O$, HNO_3? What are the equivalent weights of $Na_3PO_4 \cdot 12H_2O$, $Na_2HPO_4 \cdot 12H_2O$, and $Na_2B_4O_7 \cdot 10H_2O$ when methyl orange is the indicator? What are the equivalent weights when phenolphthalein is the indicator (in the presence of mannitol in the case of borax)? See p. 37.

16. How many milliliters of hydrochloric acid, *d* 1.12, containing 23.81 per cent HCl by weight, is required to make 2 l of one-third normal solution? Of sulfuric acid, *d* 1.84, containing 95.6 per cent H_2SO_4 by weight?

17. If 47.26 ml of HCl are equivalent to 43.56 ml of NaOH, find the value of 1 ml of the acid solution in terms of the base.

18. How much water must be added to 1 l of 0.1672 *N* sulfuric acid to make it exactly 0.1 *N*?

19. If 2.453 g of pure, anhydrous sodium carbonate react with 45.72 ml of sulfuric acid solution and 41.90 ml of the acid neutralize 44.35 ml of KOH solution, find the normality of both solutions.

20. How many milliliters of 0.3360 *N* $Ba(OH)_2$ solution are equivalent to 42.75 ml of 0.5162 *N* HCl?

CHAPTER IV

ACIDIMETRY AND ALKALIMETRY. ANALYSIS OF SODA ASH AND OXALIC ACID. SUPPLEMENTARY PROCEDURES

The useful reactions of analytical chemistry are those which take place practically completely in a given direction. Such reactions are those in which a slightly ionized substance is formed, an insoluble precipitate is obtained, a gas is evolved, or there is an oxidation of one substance at the expense of another. The law of chemical mass action applied to a reaction of the type $A + B \rightarrow C + D$ tells us that a reaction may be expected to go to completion if one of the products, either C or D, is removed as fast as it is formed, and this happens when the substance is not ionized, is insoluble, or is a gas. The reason that the reaction $NaOH + HCl = NaCl + H_2O$ takes place in dilute solutions is that water is ionized but slightly and, from the standpoint of the electrolytic dissociation theory, the reaction of neutralization is really

$$H^+ + OH^- = H_2O$$

This is shown by the fact that the heat evolved by the reaction in dilute solution is practically the same irrespective of the nature of the ions that were originally combined with the H^+ and OH^- provided that the original acid and base are both ionized almost completely.[1]

The mass-action law, applied to the ionization of water, tells us that a state of equilibrium exists when

$$\frac{[H^+] \times [OH^-]}{[H_2O]} = \text{a constant}$$

In these mass-action expressions, a symbol written inside a bracket signifies a concentration expressed in moles per liter. In the case of water, the concentration of the non-ionized H_2O is not changed appreciably as a result of ionization at room temperatures, and its concentration is enormous compared to the concentration of its ions; the above expression can be simplified, therefore, by saying $[H^+] \times [OH^-] = K_w = 1.0 \times 10^{-14}$ at 24°. This expression is of fundamental importance. It states that in any aqueous solution the concentration of hydrogen ions (expressed in moles per liter) multiplied by the concentration of the hydroxyl ions present (also expressed in moles per liter) always equals 1.0×10^{-14} at 24°.[1] Since 1 mole of H^+ and 1 mole of OH^- are formed from each mole of ionized water, it is evident that, in absolutely neutral water, the concentration of each of these ions is 1.0×10^{-7} at 24°.

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[1] Most ions are hydrated. For this reason, some textbooks insist on the use of the *hydronium* ion, H_3O^+, in place of the hydrogen ion, H^+. H_3O^+ is also called the *oxonium* ion.

Very small numbers such as these are handled conveniently with logarithms. Since the cologarithm, or *negative logarithm* as it is often called, is the logarithm of the reciprocal of a number, it can be used equally well. Usually we multiply two numbers by adding their logarithms, but we get the same answer if we subtract the negative logarithm of one from the logarithm of the other. Similarly, the value a/b can be found by adding the negative logarithm of b to the logarithm of a. If c is the concentration of H^+ ions, $\log 1/c$ or $-\log c$ is called the pH or *hydrogen exponent* of the solution. Pure water at 24° has $p\text{H} = 7$, $p\text{OH} = 7$ and $pK_w = 14$. This pH concept is widely used. In general, if the pH exceeds 7 the solution is more basic than water, and when $p\text{H} < 7$ it is more acidic than water.

Since in any solution at 24° $[H^+] \times [OH^-] = 1.0 \times 10^{-14}$, it is clear that the concentration of the OH^- is known as soon as the concentration of the H^+ is stated. In all cases $p\text{H} + p\text{OH} = 14$ at 24°.

Logarithms. Almost every reader of this book will have used logarithms in connection with the study of algebra or trigonometry, but in nearly every class of students there will be found a few who have forgotten how to use logarithms, particularly with respect to expressions like $\log 1/[H^+]$.

A logarithm of a number expresses the number as a power of some other number known as the base. Logarithms to the base 10, called *common logarithms* (Briggs), are used to simplify calculations; the expression $\log a$ always means the logarithm of the number a to the base 10 unless otherwise stated. If the number in question is an exact power of 10, it is easy to find the logarithm, as the following table shows:

Number	1,000	100	10	1	0.1	0.01	0.001
Exponential form	10^3	10^2	10^1	10^0	10^{-1}	10^{-2}	10^{-3}
Logarithm	3	2	1	0	−1	−2	−3

A logarithm is said to have two parts, the *characteristic* and the *mantissa*. The characteristic is a whole number which is written to the left of the decimal point in the logarithm, and the mantissa is the decimal fraction which is written to the right of the decimal point. The characteristic is used to locate the decimal point, and the mantissa gives the significant digits of the number. A simple example will explain this, using the number 25 with various positions of the decimal point.

Number	2500	250	25	2.5	0.25	0.025	0.0025
or	2.5×10^3	2.5×10^2	2.5×10	2.5	2.5×10^{-1}	2.5×10^{-2}	2.5×10^{-3}
Logarithm	3.3979	2.3979	1.3979	0.3979	$\bar{1}.3979$	$\bar{2}.3979$	$\bar{3}.3979$

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[1] The ionization constant of water, K_w, varies from 0.12×10^{-14} at 0° to 73×10^{-14} at 100°C. pK_w varies from 14.92 to 12.14.

Note: (*a*) When written in this way, it is a property of logarithms to the base 10 that the decimal fraction (mantissa) is always the same for a given sequence of digits; (*b*) that the characteristic of a number greater than 1 is a number which is one less than the number of digits to the left of the decimal point; and (*c*) that the characteristic of a number less than 1 indicates the decimal place where the first digit other than 0 is found. The logarithm $\bar{2}.3979$ is composed of a negative number -2 and a positive fraction 0.3979. The minus sign, therefore, applies only to the characteristic and not to the mantissa, and for that reason is written over the characteristic rather than in front of it. It is true, of course, that $-2 + 0.3979 = -1.6021$, but when the logarithm is written in this way it is not so easy to use and the advantage is lost of having the mantissa always the same for a given sequence of digits. It should be noted, however, that 2.5×10^{-2} is the same value as $10^{-1.6021}$. To avoid the difficulty of using a number like $\bar{2}.3979$ which is part negative and part positive, many people prefer to write the logarithm of 0.025 as $8.3979 - 10$ but this is likely to lead to confusion with very small numbers in which the first digit other than 0 is found more than 9 places to the right of the decimal point.

On pages at the back of the book will be found a logarithm table. From it the mantissa of any sequence of digits can be obtained. Instead of these four-place logarithms, as they are called, it is possible to construct tables which will give the mantissa to 5, 6, 7, or any desired number of decimal places. With them greater accuracy is obtained when it is desirable to use 5, 6, 7, or more significant figures in the computations, but, for the purposes of analytical chemistry, four-place logarithms are usually adequate and the larger, more bulky tables are not recommended.

If it is desired to find the logarithm of 25.62 we know in the first place that the characteristic is 1 because the number lies between the first and second powers of 10. The table of logarithms at the back of the book tells us that the mantissa of 256 is 4082, and in column two under *Proportional Parts* we find that we must add 3 to this mantissa to get the logarithm of 2562, hence log of 25.62 = 1.4085. The "proportional parts" in this table were obtained by taking the average difference between two neighboring mantissas in the same horizontal row and using a proportional part.

Antilogarithms. At the back of the book will also be found a table of *antilogarithms*. This table is used similarly to the logarithm table but from it the sequence of digits corresponding to a given mantissa is obtained.

If we wish to find the number corresponding to log = 1.4085, we turn to the table of antilogarithms at the back of the book and find that the digits corresponding to .408 are 2559; and in column five under *Proportional Parts* we find that we must add 3, which gives us the digits 2562. Since the characteristic of the logarithm is 1 we know that the desired number is 25.62.

The advantage of using logarithms lies in the fact that multiplication and division, squaring, cubing, and taking square roots, cube roots etc., become very easy processes because they are performed by additions, subtractions, multiplications, and divisions of exponents. We learned from the study of algebra that $a^n \times a^m = a^{n+m}$, and since a logarithm such as 1.4085 merely means that the original number is $10^{1.4085}$, it is clear that adding logarithms has the same effect as multiplying the original numbers. Therefore, to multiply a by b we simply add the logarithms, and to divide a by b we merely subtract the logarithm of b from the logarithm of a. To find the square of a we merely multiply its logarithm by 2 and find the antilogarithm.

Cologarithms. The cologarithm of a number is the logarithm of its reciprocal (or 1 ÷ the number). Since the logarithm of 1 is 0.0000 and the logarithm of a fraction is the logarithm of the numerator minus the logarithm of the denominator, it is evident that the cologarithm of a number is found by subtracting its logarithm from zero. Thus the log of 2 = 0.3010, and its cologarithm is $\bar{1}.6990$ (the log of 0.5 which is the reciprocal of 2). The mantissas of these cologarithms (usually called *cologs*) can be written directly from the values in the table by subtracting each digit from 9 except the last on the right (other than 0) which is subtracted from 10. In a series of multiplications and divisions it is often advantageous to use the cologarithms because adding the cologarithm has the same effect as subtracting the logarithm and the series can be carried out by a single addition of all the values. Cologarithms are sometimes called *negative* logarithms because they are obtained by subtracting the logarithms from 0.

Finding *p*H Values. From what has just been said, it is evident that pH values represent the cologarithms of hydrogen-ion concentrations expressed in moles per liter. If the hydrogen-ion concentration is an even power of 10, the pH value is at once apparent. Thus $p\text{H} = 7$ means that the hydrogen-ion concentration is 10^{-7} mole per liter. What will be the pH of a solution containing, let us say, 0.000023 mole of H^+ per liter? The logarithm of 0.000023 is $\bar{5}.36$, and the cologarithm is 4.64.[1] To find pH values corresponding to solutions containing less than 1 mole H^+ per liter, express the moles per liter as a whole number between 0 and 10 multiplied by 10 to a negative power. Then, if this number is $a \times 10^{-b}$, look up the logarithm of a in the table to two significant figures (or take it from a slide rule), and subtract this value from b.

Conversely to find the concentration in moles of H^+ per liter to correspond to $p\text{H} = 4.64$, subtract 4.64 from 0.00 and get $\bar{5}.36$, look up the number corresponding to 0.36 (=2.3), and write 2.3×10^{-5} as the desired number.

A perfectly neutral solution has a pH value of 7. If the pH value is smaller than 7, the solution can be said to be more acid than pure water, and if it is larger than 7 it is more basic. Another way of expressing this is to say that a solution is acidic if it contains more hydrogen ions per unit volume than are present in pure water and basic if it contains fewer hydrogen ions. It is well known that acids and bases vary greatly with respect to their ionization in aqueous solutions. The relative strength is shown by a comparison of the ionization constants.[2]

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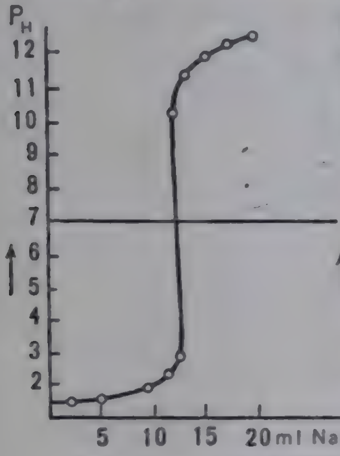
[1] This is easily seen by expressing 0.000023 as 2.3×10^{-5}. Then

$$\frac{1}{2.3 \times 10^{-5}} = \frac{10^5}{2.3} \quad \text{and} \quad \log \frac{10^5}{2.3} = \log 10^5 - \log 2.3 = 5.00 - 0.36 = 4.64.$$

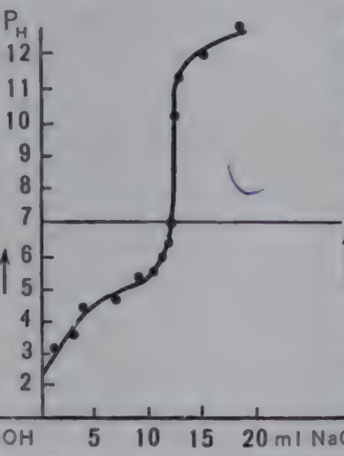
[2] The mass-action law applied to the ionization of a weak acid takes the general form $\frac{[H^+] \times [A^-]}{[HA]} = k$, in which k is called the *ionization constant*. Dibasic and tribasic acids are usually ionized to different degrees with respect to each replaceable hydrogen atom. The primary ionization constant of H_3PO_4 is $\frac{[H^+] \times [H_2PO_4^-]}{[H_3PO_4]} = 1.1 \times 10^{-2}$; the secondary ionization constant is $\frac{[H^+] + [HPO_4^{--}]}{[H_2PO_4^-]} = 2.0 \times 10^{-7}$; and the tertiary ionization constant is $\frac{[H^+] \cdot [PO_4^{---}]}{[HPO_4^{--}]} = 3.6 \times 10^{-13}$.

When a strong acid, like hydrochloric acid, is neutralized with a strong base, such as sodium hydroxide, the reaction takes place practically completely as soon as exactly one equivalent of the base has been added. There is no appreciable hydrolysis of the salt formed, and the end point takes place at $p\text{H} = 7$. It is a different matter when a weak acid like acetic acid is neutralized with sodium hydroxide. In this case the sodium acetate as it is formed tends to repress the ionization of the unneutralized acid, and when, finally, a quantity of base equivalent to the original acetic acid has been added, the pH of the solution will be distinctly higher than 7. In the same way, when sodium acetate is dissolved in water, the solution will show $p\text{H} > 7$. If a weak base like NH_4OH is neutralized with a strong acid like hydrochloric acid, the final solution will show a pH distinctly less than 7.

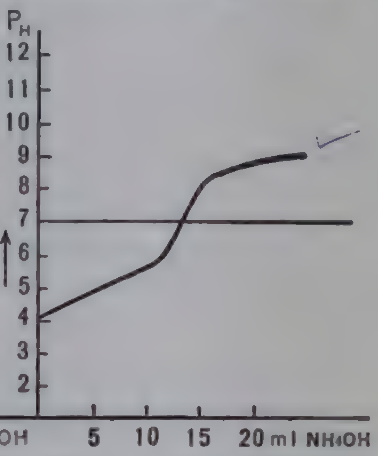
The following curves obtained by measurement of the single potential of a hydrogen electrode during a titration illustrate these points. The curve for the titration of the hydrochloric acid with sodium hydroxide shows a marked change produced by a very little base when the end point is reached. This may be taken as the halfway point of the nearly vertical line and corresponds almost exactly to $p\text{H} = 7$. The curve for the titration of the acetic acid shows a distinct rise in pH long before the end point is reached, and the halfway point of the nearly vertical line is



Titration of 0.1 N HCl with 0.1 N NaOH



Titration of 0.1 N $HC_2H_3O_2$ with 0.1 N NaOH



Titration of 0.1 N $HC_2H_3O_2$ with 0.1 N NH_4OH

The value 3.6×10^{-13} for the tertiary ionization of phosphoric acid shows that the presence of a considerable quantity of HPO_4^{-} in an aqueous solution does not increase very much the concentration of the hydrogen ions present over the quantity furnished as a result of the ionization of water itself.

The mass-action law applied to the ionization of a *strong acid* or of a *strong base* does not give a useful value because, if the ionization is practically complete, the value of the ionization constant approaches ∞. In comparing the ionization constants, therefore, it is customary to call that of the strong acids and bases [1]; the number is enclosed in brackets to show that it is not obtained by a rigid application of the mass-action law.

at a $pH > 7$. The third curve shows an indistinct end point, although the solution is neutral with $pH = 7$ when an equivalent of base has been added. The indistinct end point is due to the fact that the ionization of both acid and the base is slight in the presence of their neutral salt; as a result, ammonium acetate is hydrolyzed appreciably in aqueous solution.

From what has just been said four conclusions can be drawn: (1) the end point of a titration of an acid with a base does not always coincide with $pH = 7$; (2) a good end point cannot be obtained if both the acid and the base are weak; (3) when a weak acid is titrated with a strong base, the end point occurs at $pH > 7$; and (4) when a weak base is titrated with a strong acid the end point occurs at $pH < 7$.

INDICATORS

The indicators used in acidimetry and alkalimetry are dyestuffs which are of one color in acid solutions and another color in basic solutions. They are, as a rule, weak acids, though some of them are weak bases. It has been found that in organic compounds the color can usually be traced to a particular arrangement of atoms called a *chromophor*. The change in color, therefore, is caused by a slight rearrangement of the atoms in the molecule. Thus, if the salt of an indicator acid is yellow and on treatment with acid it turns red, the change in color is due to the fact that, when the indicator acid is liberated by the action of the stronger acid, the molecule undergoes a slight change in the way the atoms are linked together and thereby loses temporarily the ability to ionize as an acid. It is not sufficient, however, to assume that this change of color is caused solely by the fact that the ions have a color other than that of the undissociated molecule; on the contrary, it has been shown in certain cases that the ions have the same color that the undissociated molecule has before the rearrangement of the atoms in the molecule has taken place. On the other hand, as regards the proper use of indicators it is necessary simply to bear in mind how salts of weak acids behave in the presence of stronger acids and how the acids themselves behave in the presence of alkali.

By means of electrometric tests it is possible to determine the hydrogen-ion concentration at which any indicator changes color. Indicators are known which change at different concentrations of hydrogen ion, and for any special case an indicator should be chosen which will change color as nearly as possible at the hydrogen-ion concentration corresponding to the saturation point of the acid and base used in the analysis.

Indicators may be classed as *neutral* when they change color at about pH 7, *sensitive to acids* when the transition interval is distinctly greater than pH 7, and *sensitive to bases* they change color at values distinctly below pH 7. With absolutely pure water, containing no dissolved CO_2, the first class show the transition tint, the second class show their acid colors, and the third show their basic tints. In other words, water is neutral to the first, acid to the second, and basic to the third class. Water saturated with CO_2 under a pressure of 1 atmosphere of this gas has a pH of about 3.7 at 25°; water in contact with a normal atmosphere containing about 0.03 per cent by volume of CO_2 has a pH of about 5.7; and carefully prepared conductivity water has a pH close to 7.

Innumerable organic compounds containing acid or basic groups change color at definite concentrations of H^+, and it is possible to select indicators so that a fairly close estimation of the pH can be made from pH 1 to pH 14. The following table shows the color-change intervals of some of the most-used indicators. Some indicators, like thymol blue, have two transitions because of the presence of more than one group sensitive to acid or base.

COLOR–CHANGE INTERVALS OF CERTAIN ACID–BASE INDICATORS AT 25°

Chemical Name	Trade Name	Color Change Acid-Base	pH Range
Thymolsulfonphthalein	Thymol blue	Red-yellow	1.2– 2.8
Diphenylamino-*p*-benzene sodium sulfonate	Tropeoline 00	Red-yellow	1.3– 3.0
Dimethylaminoazobenzene	Methyl yellow	Red-yellow	2.9– 4.0
Tetrabromophenolsulfonphthalein	Bromophenol blue	Yellow-purple	3.0– 4.6
Dimethylaminoazobenzene sodium sulfonate	Methyl orange	Red-orange yellow	3.1– 4.4
Tetrabromophenol-*m*-cresolsulfonphthalein	Bromocresol green	Yellow-blue	3.9– 5.4
Dimethylaminoazobenzene-*o*-carboxylic acid	Methyl red	Red-yellow	4.2– 6.2
Dichlorosulfonphthalein	Chlorophenol red	Yellow-red	4.8– 6.4
Dibromothymolsulfonphthalein	Bromothymol blue	Yellow-blue	6.0– 7.6
Phenolsulfonphthalein	Phenol red	Yellow-red	6.4– 8.0
Dimethyldiaminophenazine chloride	Neutral red	Red-yellow-orange	6.8– 8.0
m-Cresolsulfonphthalein	*m*-Cresol purple	Yellow-purple	7.4– 9.0
Thymolsulfonphthalein	Thymol blue	Yellow-blue	8.0– 9.6
Phenolphthalein	Phenolphthalein	Colorless-red	8.0– 9.8
Thymolphthalein	Thymolphthalein	Colorless-blue	9.3–10.5
Na salt of *p*-nitraniline-azosalicylic acid	Alizarin yellow	Yellow-violet	10.1–12.0

Suitable indicator solutions contain 0.05–0.1 g of the solid in 100 ml of solution. Tropeoline 00, methyl orange, and alizarin yellow can be dissolved in water. Methyl yellow, neutral red, phenolphthalein, and thymolphthalein are soluble in 90 per cent alcohol. The sulfonphthaleins dissolve in water after an equivalent quantity of sodium hydroxide has been added to form the water-soluble sodium salt. Triturate 0.1 g of the powder with the following volumes of 0.1 *N* NaOH; thymol blue, 2.15 ml; bromophenol blue, 1.5 ml; bromocresol green, 1.45 ml; methyl red, 3.7 ml; chlorophenol red 2.35 ml; bromothymol blue, 1.6 ml; phenol red, 2.85 ml; cresol purple, 2.6 ml. Dissolve in water and dilute to 100 ml.

It was stated on p. 50 that some indicators changed color at *p*H values distinctly below 7 and were sensitive to weak bases, others changed at about *p*H 7, and others changed at *p*H distinctly greater than 7. This, however, does not mean that the indicators themselves are acid, neutral, or basic in such a grouping. Some indicators contain both acid and basic groups in their molecules. Methyl orange, which changes color at *p*H 3.1–4.4, is an acid which is stronger than acetic acid; phenolphthalein is an acid comparable in strength to boric acid; methyl orange is sensitive to bases, and phenolphthalein to acids. Methyl yellow is a weak base with ionization constant 1×10^{-11}. As a general rule, the fact that an indicator is sensitive to bases and changes color at a *p*H below 7 indicates that the indicator itself is either a relatively strong acid or a weak base. Some writers call methyl orange a weak base and others classify it as an acid. The dimethylaminoazobenzene sulfonic acid itself is distinctly acidic for the SO_3H group is much stronger as an acid than the substituted amino group as a base, but the sodium salt of dimethylaminoazobenzene sulfonic acid behaves like a weak base. It is a base in the sense that any salt of a weak acid, like sodium acetate for example, is a weak base, and, as a matter of fact, the Brönsted definition of acid and base does make the acetate ion a base. It is idle, therefore, to argue whether the different indicators are themselves acids or bases. Many of them are weak acids which are present as sodium salts in the indicator solutions.

It is sometimes desirable to have at hand solutions of definite *p*H values. These so-called *buffer solutions* can be prepared from carefully standardized 0.2 *N* HCl, 0.1 *N* HCl, 0.1 *N* NaOH, and 0.1 *M* solutions of potassium acid phthallate, monopotassium phosphate, potassium chloride, and boric acid. To prepare 100 ml of the last four solutions, dissolve separately 2.042 g $KHC_8H_4O_4$, 1.362 g KH_2PO_4, 0.746 g KCl, and 0.62 g H_3BO_3 in water, dilute each solution to exactly 100 ml in a volumetric flask, mix, and store in glass-stoppered bottles. To prepare solutions of definite pH mix these solutions in accordance with the following table.[1]

For a rapid and approximate determination of the pH a so-called *universal indicator* can be used. Universal indicators are mixtures of dyestuffs so chosen that the mixture assumes a different color at each different unit of pH. Thus Kolthoff has recommended a mixture of 15 ml 0.1 per cent dimethylaminoazobenzene + 5 ml of 0.1 per cent methyl red + 20 ml 0.1 per cent bromothymol blue + 20 ml of 0.1 per cent phenolphthalein + 20 ml of 0.1 per cent thymolphthalein. The colors

COMPOSITION AND pH OF CLARK AND LUBS BUFFER MIXTURES AT 20°

Composition	pH
48.5 ml 0.2 N HCl + 25 ml 0.2 N KCl diluted to 100 ml................	1.0
32.25 “ “ “ “ “ “ “ “ “	1.2
20.75 “ “ “ “ “ “ “ “ “	1.4
13.15 “ “ “ “ “ “ “ “ “	1.6
8.3 “ “ “ “ “ “ “ “ “	1.8
5.3 “ “ “ “ “ “ “ “ “	2.0
3.35 “ “ “ “ “ “ “ “ “	2.2
46.70 ml 0.1 N HCl + 50 ml 0.1 M $KHC_8H_4O_4$ diluted to 100 ml..........	2.2
39.60 “ “ “ “ “ “ “ “ “	2.4
32.95 “ “ “ “ “ “ “ “ “	2.6
26.42 “ “ “ “ “ “ “ “ “	2.8
20.32 “ “ “ “ “ “ “ “ “	3.0
14.70 “ “ “ “ “ “ “ “ “	3.2
9.90 “ “ “ “ “ “ “ “ “	3.4
5.97 “ “ “ “ “ “ “ “ “	3.6
2.63 “ “ “ “ “ “ “ “ “	3.8
0.40 ml 0.1 N NaOH + 50 ml 0.1 M $KHC_8H_4O_4$ diluted to 100 ml........	4.0
3.70 “ “ “ “ “ “ “ “ “	4.2
7.50 “ “ “ “ “ “ “ “ “	4.4
12.15 “ “ “ “ “ “ “ “ “	4.6
17.70 “ “ “ “ “ “ “ “ “	4.8
23.85 “ “ “ “ “ “ “ “ “	5.0
29.95 “ “ “ “ “ “ “ “ “	5.2
35.45 “ “ “ “ “ “ “ “ “	5.4
39.85 “ “ “ “ “ “ “ “ “	5.6
43.00 “ “ “ “ “ “ “ “ “	5.8
45.45 “ “ “ “ “ “ “ “ “	6.0
5.70 ml 0.1 N NaOH + 50 ml 0.1 M KH_2PO_4 diluted to 100 ml..........	6.0
8.60 “ “ “ “ “ “ “ “ “	6.2
12.60 “ “ “ “ “ “ “ “ “	6.4
17.80 “ “ “ “ “ “ “ “ “	6.6
23.65 “ “ “ “ “ “ “ “ “	6.8

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[1] W. M. Clark, *The Determination of Hydrogen Ions*, 3rd ed., 1928.

Composition	pH
29.63 ml. 0.1 N NaOH + 50 ml 0.1 M KH_2PO_4 diluted to 100 ml	7.0
35.00 " " " " " " " " "	7.2
39.50 " " " " " " " " "	7.4
42.80 " " " " " " " " "	7.6
45.20 " " " " " " " " "	7.8
46.80 " " " " " " " " "	8.0
2.61 ml 0.1 N NaOH + 50 ml 0.1 M H_3BO_3 diluted to 100 ml	7.8
3.97 " " " " " " " " "	8.0
5.90 " " " " " " " " "	8.2
8.50 " " " " " " " " "	8.4
12.00 " " " " " " " " "	8.6
16.30 " " " " " " " " "	8.8
21.30 " " " " " " " " "	9.0
26.70 " " " " " " " " "	9.2
32.00 " " " " " " " " "	9.4
36.85 " " " " " " " " "	9.6
40.80 " " " " " " " " "	9.8
43.90 " " " " " " " " "	10.0

obtained when 0.1 ml of the mixture is added to 10 ml of the solution to be tested are: rose at pH 2.0; reddish orange at pH 3.0; orange at pH 4.0; yellow-orange at pH 5.0; lemon-yellow at pH 6.0; yellow-green at pH 7.0; green at pH 8.0; blue-green at pH 9.0; and violet at pH 10. Such mixtures can be purchased but are not very accurate.

The indicators most used in quantitative analysis are *methyl orange*, *methyl red*, and *phenolphthalein*.

1. Methyl Orange

By methyl orange,[1] Lunge,[2] who first proposed the use of this indicator, understood either the free sulfonic acid of dimethylaminoazobenzene or its sodium or ammonium salt.

In the free state, the sulfonic acid is obtained in the form of reddish violet scales, soluble in considerable water. If some of the solid is dissolved in as little water as possible, a distinct reddish orange solution is obtained; but on the further addition of water this color gradually changes to yellow. If a trace of an acid is added to the yellow solution, it becomes red again, and on further dilution with water the color changes to orange and finally to yellow once more, if too much acid was not added. The color changes which take place between $p\text{H} = 3.1\text{–}4.4$ can be easily explained.

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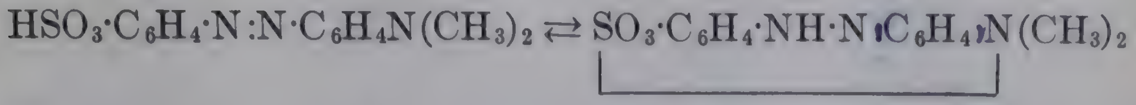
[1] This dyestuff has been known commercially as helianthin, orange III, tropäolin D, Poirrier's orange III, dimethylaniline orange, mandarine orange, and gold orange.

[2] *Ber.*, **1878**, II, 1944; *Chem. Ind.*, **1881**, 348; *Handbuch für Sodaindustrie*, I, 52 (1879); II, 151 (1893).

In the sensitive neutral solution there is a condition of equilibrium between two isomeric forms of methyl orange as expressed by the equation:



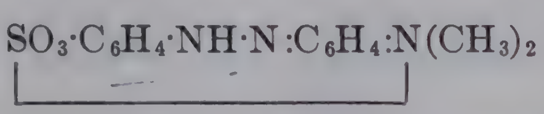
$$HSO_3{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4N(CH_3)_2 \rightleftarrows SO_3{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}C_6H_4{:}N(CH_3)_2$$

The formula on the left represents the yellow substance and the color is due to the azo group N:N, whereas the formula on the right represents the red substance which has for its chromophor the quinoid group $:C_6H_4:$. The formula on the left has a sulfonic group which imparts acid properties to the molecule, and at the other end is an $N(CH_3)_2$ group which has weakly basic properties. The formula on the right, therefore, represents an inner salt inasmuch as the acid- and base-forming groups are united.

The sodium salt of methyl orange is yellow and has the formula

$$NaSO_3{\cdot}C_6H_4N{:}NC_6H_4N(CH_3)_2$$

and when decomposed by acids the free sulfonate at once reverts to the red form:[1]



$$SO_3{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}C_6H_4{:}N(CH_3)_2$$

Methyl orange is an excellent indicator for weak bases but cannot be used for the titration of weak acids.

If it is desired to titrate a solution containing sodium hydroxide with a tenth-normal acid, add a little methyl orange to the alkaline solution and titrate with acid unit the solution is colored a distinct red. This color will not appear permanently until an excess of the acid has been added. The use of excess acid causes a slight error in the analysis which is greater in proportion to the amount of indicator employed, and to the dilution of the solution.

From what has been said the following rule holds:

In any titration a small amount of indicator should be used, and, inasmuch as the change of color is proportional to the concentration and not to the absolute amount of acid present, the analyzed solution should have as nearly as possible the same concentration as prevailed in the standardization of the reagent used.

If a normal acid is used for the titration, the change of color is very sharp when the volume of the solution titrated amounts to about 100 ml. Even with a fifth-normal solution the change of color is very distinct, but less so with tenth-normal solutions; but these can be titrated provided the standardization was made at the same dilution as that used in the analysis.

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[1] Cf. Stieglitz, *J. Am. Chem. Soc.*, **25**, 1117; Peters and Redmon, *J. Chem. Education*, **17**, 525 (1940).

How is it with the end point in the titration of an acid with an alkali hydroxide solution?

If a few drops of methyl orange are added to 100 ml of water, the water will be colored distinctly yellow. If the solution contains the same amount of hydrochloric acid as is contained in 10 ml of a tenth-normal solution of this acid, the solution will be colored a deep red. In order that the solution shall assume its original yellow color, it is only necessary to add exactly 10 ml of 0.1 N alkali hydroxide solution, but no excess of alkali, because the water is itself sufficient to decompose the dyestuff sufficiently to produce the yellow color.

It is evident, then, that it is not a matter of indifference in the analysis whether the titration is completed by the addition of acid or by the addition of alkali. In the former case, for the titration of T ml of 0.1 N alkali solution, $T + t$ ml of 0.1 N acid would be necessary.

Methyl orange is more sensitive toward alkali than toward acid, but many prefer to finish the titration by the addition of acid, for most eyes can detect the change from yellow to red with greater accuracy. In principle it is more accurate to accomplish the titration the other way, as was recommended by F. Glaser.

Uses. Methyl orange is suitable for the titration of strong acids (HCl, HNO_3, H_2SO_4) as well as phosphoric and sulfurous acids. Hydrochloric and nitric acids can be titrated with this indicator with a sharper end point than sulfuric acid.

Phosphoric Acid. If free phosphoric acid is titrated with sodium hydroxide in the presence of this indicator, the solution changes from red to yellow when one-third of the phosphoric acid has been neutralized:

$$H_3PO_4 + OH^- = H_2PO_4^- + H_2O$$

The primary phosphates are neutral toward methyl orange; the secondary and tertiary phosphates react alkaline toward it. With half-normal solutions, the end point of the reaction is fairly sharp. With tenth-normal solutions it is less so, and an excess of about 0.3 ml of the 0.1 N alkali hydroxide is necessary to cause the change from red to yellow.

Sulfurous Acid. In titrating sulfurous acid with sodium hydroxide, the yellow color is obtained when half the acid has been neutralized

$$H_2SO_3 + OH^- = HSO_3^- + H_2O$$

and HSO_3^- is neutral toward this indicator.

The weak acids HCN, H_2CO_3, H_2S, H_3AsO_3, H_3BO_3, and $HCrO_4^-$ when present in moderate quantities do not affect the color of methyl orange solutions. CO_2 and H_2S produce an orange-red coloration only when present in large amounts. For this reason dilute solutions of the alkali salts of these acids can be titrated with accuracy by means of this indicator.

Organic acids cannot be titrated with methyl orange.

The strong and weak bases $NaOH$, KOH, NH_4OH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, and $Mg(OH)_2$ can be titrated with great accuracy by means of this indicator, and the same is true of the amine bases (methyl and ethyl amines, etc.); on the other hand, such weak bases as pyridine, aniline, and toluidine cannot be titrated.

Nitrous acid ordinarily cannot be titrated with this indicator because the acid destroys it. If, however, an excess of alkali is first added to the solution of nitrous acid, then the methyl orange, the titration can be accomplished with accuracy.

2. Methyl Red

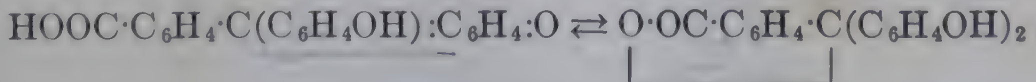
$$(CH_3)_2\overset{4}{N} - C_6H_4 - \overset{1}{N} = \overset{2}{N} - C_6H_4 - \overset{1}{C}OOH$$

Paradimethylaminoazobenzene-o-carboxylic acid

This valuable indicator is suitable for titrating weak organic bases and ammonia. The aqueous solution of methyl red is orange, but, if a few drops are added to 50–100 ml of water, the water is colored a pale yellow. The addition of a drop of 0.1 *N* HCl at once turns the liquid a violet-red without its passing through any intermediate shade, and by the addition of a drop of ammonia the solution becomes nearly colorless again. Methyl red is not very sensitive toward carbonic acid, but more so than methyl orange, so that it is less suitable for the titration of carbonates. The chief advantage of this indicator lies in the sharp color change from a very pale yellow to a violet-red, even in titrating ammonia. The color change is at pH = 4.2–6.2.

3. Phenolphthalein

Phenolphthalein is a very weak acid forming red salts which contain the strongly chromophoric quinoid group: C_6H_4:. The free acid, however, is unstable and, when set free from one of its colored salts, by the addition of acid, it reverts instantly into a colorless lactoid form, containing no chromophor group:



$$HOOC\cdot C_6H_4\cdot C(C_6H_4OH):C_6H_4:O \rightleftarrows O\cdot OC\cdot C_6H_4\cdot C(C_6H_4OH)_2$$

red in basic med.

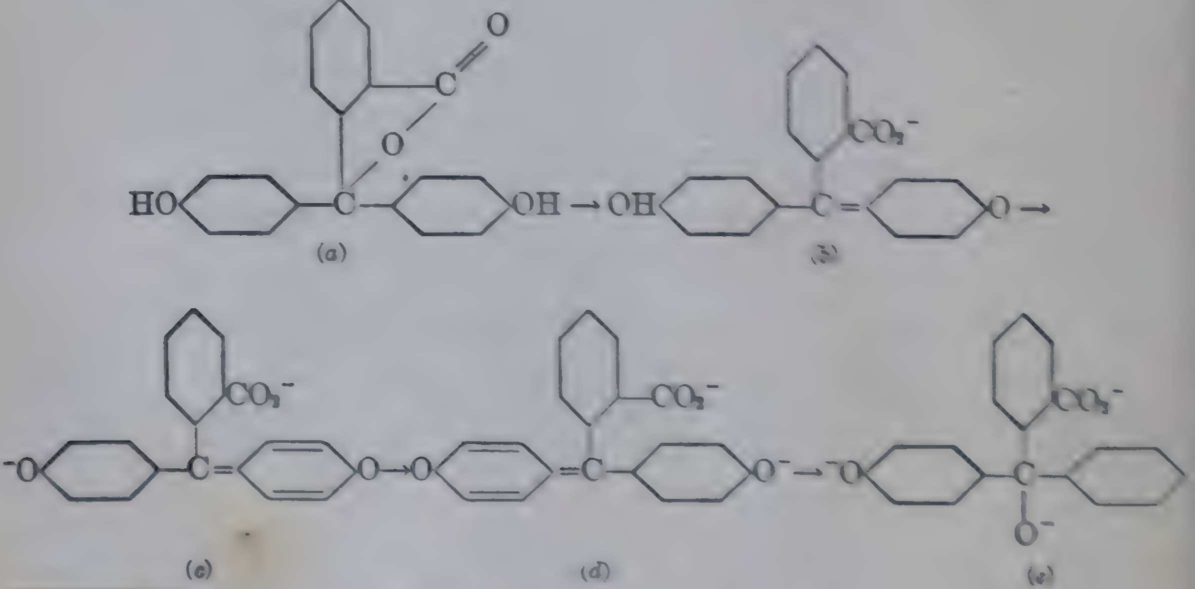
colorless in acidic med.

In the free acid, therefore, the condition of equilibrium favors the lactoid form and only traces of the quinoid acid are present. This trace of quinoid acid is ionized somewhat and is in equilibrium with its ions:

$$\mathrm{HOOC{\cdot}C_6H_4{\cdot}C(C_6H_4OH){:}C_6H_4{:}O} \rightleftarrows \mathrm{H^+ + OOC{\cdot}C_6H_4{\cdot}C(C_6H_4OH){:}C_6H_4{:}O^-}$$

The addition of an alkali causes the hydrogen ions to disappear, so that more of the quinoid molecules must be ionized to preserve equilibrium, and the quinoid molecules in turn are reproduced from the lactoid as fast as the former are converted into the salt. Phenolphthalein is a very sensitive indicator towards acids, but on account of being a very weak acid it does not form stable salts with weak bases.

Phenolphthalein becomes pink in solutions of pH greater than 8.3 but becomes colorless in solutions which contain a large excess of alkali hydroxide. Potentiometric titrations indicate that phenolphthalein is tribasic and that the colorless forms are shown by free phenolphthalein and by the ion of tribasic salt. These facts and the theory that the color is due to *resonance*, or vibration in the molecule, can be explained as follows.[1] Phenolphthalein in the unneutralized state has a colorless molecule that can be represented by the formula shown below in (*a*). The addition of OH^- causes the formation of H_2O with one of the phenol groups, but this causes disruption of the lactone group and the negative charge on the anion formed shifts to the carboxyl group giving the compound shown at (*b*). But the second phenol group is about as strongly acidic as the other, and it reacts with a second molecule of OH^- before the first reaction is completed, and this results in the formation of the dibasic anion shown in (*c*). The part of the compound containing the two phenol groups is now symmetrical, and the two resonance forms are shown in (*c*) and (*d*). The addition of strong caustic alkali forms the tribasic salt of phenolphthalein, and the colorless tribasic anion shown in (*e*) results in which no resonance is possible.



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[1] Peters and Redmon, *J. Chem. Education*, **17**, 525 (1940).

Uses. Phenolphthalein is particularly suited for the titration of organic and inorganic acids and strong bases, but not for the titration of ammonia.

If the red-colored solution containing phenolphthalein and a little alkali is treated with an excess of concentrated alkali hydroxide solution, the red color disappears at $pH = 10$ but returns if the solution is diluted with water. Phenolphthalein, therefore, cannot be used as an indicator for the titration of concentrated alkali without previous dilution with water.

Phenolphthalein is a sensitive indicator toward acids. It is far more sensitive to acids than is methyl orange, for not only can the presence of weak acids be detected, but even very small amounts can be titrated with accuracy.

Ordinary distilled water usually contains carbon dioxide, as can be shown by slowly adding 0.1 N barium hydroxide solution, drop by drop, to 100 ml of water containing a drop of the indicator solution. Where the alkali first meets the water, a red color is produced which disappears on stirring, so that often as much as 0.5 to 1.8 ml of the alkali must be added before a permanent red color is obtained. The disappearance of the red shows the presence of acid (in this case carbonic acid), and its amount corresponds to the alkali neutralized.

Phosphoric Acid. If a solution of phosphoric acid containing phenolphthalein is titrated with normal sodium hydroxide solution, a permanent coloration is produced when two-thirds of the phosphoric acid is neutralized:

$$H_3PO_4 + 2OH^- \rightarrow HPO_4^{--} + 2H_2O$$

Apparently Na_2HPO_4 reacts neutral toward phenolphthalein, but this is not quite correct, for a pure solution of disodium phosphate is colored a pale pink by phenolphthalein, and on dilution with water the intensity of the color increases owing to progressive hydrolysis:

$$HPO_4^{--} + H_2O \rightleftarrows OH^- + H_2PO_4^-$$

During the titration of phosphoric acid with sodium hydroxide, a pale pink color is obtained somewhat too soon, and this color gradually increases in intensity until finally a maximum is reached, which is taken as the end point. It is possible that this hydrolysis could be prevented by the addition of a large excess of sodium chloride and cooling to about 0°C.

Carbonic Acid. If the solution of a neutral alkali carbonate is treated with phenolphthalein a red color is obtained, showing the presence of hydroxyl ions in the solution, due to hydrolysis:

$$CO_3^{--} + H_2O \rightleftarrows OH^- + HCO_3^-$$

If hydrochloric acid is added to such a solution which is not too dilute and is at a temperature of 0°, decolorization is effected when the alkali carbonate[1] is changed to bicarbonate. At ordinary temperatures a sharp end point cannot be obtained; the color gradually fades. Pure sodium bicarbonate dissolved in ice-cold water is not colored by the addition of phenolphthalein; if it is warmed to the temperature of the room it turns red, but on cooling the color disappears (Küster).

Silicic acid seems to be without influence upon phenolphthalein, for alkali silicates (the water-glasses) can be titrated with accuracy.

Chromic acid and acid chromates are changed by the addition of alkali to neutral chromates, which have no action upon phenolphthalein.

Alkali aluminates can be titrated accurately with this indicator, for aluminum hydroxide does not affect it.

Uses of Indicators. Indicators are used for two distinct purposes: (1) to show the actual concentrations of hydrogen ions in dilute solutions of acids and bases; and (2) to show the end point of a titration. The actual concentration of hydrogen ions depends upon the quantity of acid present and upon the extent to which the acid is ionized. A tenth-normal solution of acetic acid requires just as much sodium hydroxide to neutralize it as the same volume of tenth-normal hydrochloric acid, but the hydrochloric acid contains about 70 times as many hydrogen ions. The tenth-normal acetic acid has a pH value of about 2.9, and the hydrochloric acid a pH value of about 1. For many purposes it is much more important to know the pH value of a solution than the actual content of acid molecules.

The concentration of hydrogen ions, or the corresponding pH value, of a dilute solution or an acid or of a base can be computed easily from the so-called *ionization constant* of the acid or base. The ionization of a weak acid can be regarded as a chemical reaction that quickly reaches a state of equilibrium. Thus, if HA represents any weak acid, H^+ the hydrogen ion, and A^- the anion, the ionization reaction is

$$HA \rightleftarrows H^+ + A^-$$

and the mass-action expression corresponding to this reaction is $[H^+] \times [A^-]/[HA] = k$. In such cases $[H^+]$, $[A^-]$, and $[HA]$ are usually expressed in moles per liter, and the concentrations are those corresponding to a state of equilibrium.

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[1] Alkaline-earth carbonates behave differently. They do not dissolve appreciably until the solution has a pH smaller than 6. Cf. pp. 76, 81.

The stronger the acid, the larger the ionization constant. For a completely ionized acid, the ionization constant is assumed to be 1, cf. p. 49. The mass-action law does not help us much when the ionization is practically complete. When expressing concentrations in moles per liter we assume that one unit of a binary electrolyte gives two, and this leads to a mathematical error because the units are not absolutely the same. Such an error, however, can be disregarded in working with weak electrolytes.

In considering the ionization of acids with more than one replaceable hydrogen, such as sulfuric or phosphoric acid, the ionization reactions should never be written $H_2SO_4 \rightleftarrows 2H^+ + SO_4^{--}$ or $H_3PO_4 \rightleftarrows 3H^+ + PO_4^{---}$ because the first equation states that one sulfate anion is formed for every two hydrogen ions and the second equation states that one phosphate is formed for every three hydrogen ions. This is false. The ionization of sulfuric acid takes place in two stages and of phosphoric acid in three stages.

$$H_2SO_4 \rightleftarrows H^+ + HSO_4^- \qquad H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$$

$$HSO_4^- \rightleftarrows H^+ + SO_4^{--} \qquad H_2PO_4^- \rightleftarrows H^+ + HPO_4^{--}$$

$$HPO_4^{--} \rightleftarrows H^+ + PO_4^{---}$$

The corresponding mass-action expressions are

$$\frac{[H^+][HSO_4^-]}{[H_2SO_4]} = K_1 = [1] \qquad \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = K_1 = 1.1 \times 10^{-2}$$

$$\frac{[H^+][SO_4^{--}]}{[HSO_4^-]} = K_2 = 3 \times 10^{-2} \qquad \frac{[H^+][HPO_4^{--}]}{[H_2PO_4^-]} = K_2 = 2.0 \times 10^{-7}$$

$$\frac{[H^+][PO_4^{---}]}{[HPO_4^{--}]} = K_3 = 3.6 \times 10^{-13}$$

In the case of phosphoric acid, we may consider that three acids are present. The first, H_3PO_4, corresponds to a moderately strong acid and is about 35 per cent ionized in tenth-normal solution; the second is weak and will not show an acid reaction to methyl orange; the third is an extremely weak acid. We can multiply the three equilibrium expressions together and get $\frac{[H^+]^3 \times [PO_4^{---}]}{[H_3PO_4]} = K_1 \times K_2 \times K_3 = 7.9 \times 10^{-22}$, which is precisely the same form of expression that we would get if the reaction $H_3PO_4 \rightarrow 3H^+ + PO_4^{---}$ took place, but in substituting numerical values we must remember that the quantities of H^+ formed by the secondary and tertiary ionization are inappreciable with respect to that formed by the primary ionization. The value of $[PO_4^{---}]$ would be merely that extremely low concentration formed by the tertiary ionization. The only significance of the expression $K_1 \times K_2 \times K_3$ is to show the effect that increasing the H^+ concentration has upon that of the PO_4^{---}. This explains, for example, why phosphates dissolve readily in solutions of HCl or HNO_3.

The following table shows the ionization constants of some acids and bases.

ACIDS		K_a	$p_a = -\log K_a$
Acetic		1.8×10^{-5}	4.74
Arsenic, K_1		5.0×10^{-3}	2.30
Benzoic		6.8×10^{-5}	4.16
Boric		6.0×10^{-10}	9.22
Carbonic	K_1	4.9×10^{-7}	6.31
	K_2	6.3×10^{-11}	10.20
Chromic, K_1		6.0×10^{-7}	6.22
Citric	K_1	8.0×10^{-4}	3.10
	K_2	5.0×10^{-5}	4.30
	K_3	2.0×10^{-6}	5.70
Formic		2.0×10^{-4}	3.70
Hydrogen cyanide		7×10^{-10}	9.14
Hydrogen sulfide	K_1	9×10^{-8}	7.05
	K_2	1.2×10^{-15}	14.92
Oxalic	K_1	3.8×10^{-2}	1.42
	K_2	3.5×10^{-5}	4.46
Phosphoric	K_1	1.1×10^{-2}	1.96
	K_2	2.0×10^{-7}	6.70
	K_3	3.6×10^{-13}	12.44
Sulfuric, K_2		3.0×10^{-2}	1.52
Sulfurous	K_1	1.7×10^{-2}	1.77
	K_2	1.0×10^{-7}	7.00
Tartaric	K_1	9.7×10^{-4}	3.01
	K_2	9.0×10^{-5}	4.05
Trichloroacetic		1.3×10^{-1}	0.88

BASES	K_b	$p_b = -\log K_b$
Ammonia	1.75×10^{-5}	4.76
Barium hydroxide, K_2	3×10^{-2}	1.52
Ethylamine	5.6×10^{-4}	3.25
Hydrazine	3.0×10^{-6}	5.52

Let us now take some concrete examples to show how the approximate pH value of a solution can be computed when the ionization constant of the acid or base is known.

Example 1. What is the approximate pH of a solution of 0.012 N hydrochloric acid? We assume that the acid is completely ionized and the concentration of hydrogen ions in moles per liter is 1.2×10^{-2}. The log of $1.2 = 0.08$. $\text{Log}\,\dfrac{1}{1.2 \times 10^{-2}} = \log \dfrac{10^2}{1.2} = 2 - 0.08 = 1.92 = p\text{H}$.

Example 2. What is the approximate pH of 0.012 N acetic acid? This is a simple problem in algebra. Since acetic acid when it ionizes yields an equal quantity of hydrogen and acetate ions, we can say that x represents the concentration of hydrogen ions and of acetate ions and the undissociated acetic acid will have the concentration $0.012 - x$ when equilibrium is reached. The above table of ionization constants gives the value of 1.8×10^{-5} for acetic acid. Using the symbol AcO^- for the acetate anion and HAcO for acetic acid, as recommended by the American Chemical Society, we have

$$\frac{[\text{H}^+] \times [\text{AcO}^-]}{[\text{HAcO}]} = \frac{x^2}{0.012 - x} = 1.8 \times 10^{-5}$$

Such an expression is a little awkward to handle because of the small coefficient of x when we expand it. Since we are working with only two significant figures and the ionization of acetic acid is less than 5 per cent, we will introduce no appreciable error if we call the concentration of the undissociated acetic acid 0.012 instead of $0.012 - x$. We have also neglected, in the numerator of the above fraction, the small quantity of hydrogen ions produced by the ionization of water itself. This was permissible because it would not affect the second significant figure. Our simplified equation is, therefore,

$$\frac{[\mathrm{H}^+] \times [\mathrm{AcO}^-]}{[\mathrm{HAcO}]} = \frac{x^2}{0.012} = 1.8 \times 10^{-5}$$

$$x^2 = 22 \times 10^{-8}$$

$$x = 4.5 \times 10^{-4} \text{ corresponding to } p\mathrm{H} = 3.35$$

Example 3. What is the pH of a solution of 0.012 N acetic acid which contains 8.0 g of $NaC_2H_3O_2 \cdot 3H_2O$ *in 100 ml of the solution?*

This problem becomes easy if we make three assumptions. (1) The concentration of the hydrogen ions is x. (2) The concentration of the undissociated acetic acid is approximately 0.012 because the value x was estimated to be 4.5×10^{-4} in *Example 2* and it will be much smaller in the presence of sodium acetate. (3) The concentration of the acetate ion is $80 \div 136 = 0.59$ mole per liter if we assume that the sodium acetate is completely ionized. This value will not be changed appreciably by the very small quantity of acetate ions formed by the ionization of the acetic acid.

We have, therefore,

$$\frac{[\mathrm{H}^+][\mathrm{AcO}]}{[\mathrm{HAcO}]} = \frac{0.59x}{0.012} = 1.8 \times 10^{-5}$$

$$x = 3.7 \times 10^{-7} \text{ corresponding to } p\mathrm{H} = 6.43$$

Example 4. Compute the approximate pH of a solution of 100 ml of 0.012 N HCl to which 8.0 g of $NaC_2H_3O_2 \cdot 3H_2O$ *has been added.* Here 0.059 mole of acetate has been added to 0.0012 mole of HCl; the solution contains after the neutralization 0.012 mole of practically undissociated HAcO and 0.0578 mole of excess acetate ions in 100 ml. Expressed in moles per liter:

x = concentration of hydrogen ions
0.578 = concentration of acetate ions
0.012 = concentration of undissociated acetic acid

Then

$$\frac{[\mathrm{H}][\mathrm{AcO}]}{[\mathrm{HAcO}]} = \frac{0.578x}{0.012} = 1.8 \times 10^{-5}$$

$$x = 3.8 \times 10^{-7} \qquad p\mathrm{H} = 6.43$$

These examples illustrate how the approximate pH of acid solutions can be computed. The values can be checked by means of the indicators listed on p. 51. The last two problems show how the salt of a weak acid acts as a *buffer* and keeps the hydrogen-ion concentration low even when an appreciable quantity of strong acid is added to a solution.

Example 5. What is the approximate pH value of a solution of 0.012 N ammonia? What is the pH of the same solution after it is made 0.59 M in ammonium salt? The ionization constant of the equilibrium $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ is usually written $[NH_4^+][OH^-]/[NH_3] = 1.8 \times 10^{-5}$. This constant has the same value as acetic acid. Since the concentrations of ammonia and ammonium salt correspond to those of acetic acid and sodium acetate used in *Examples 2 and 3*, corresponding mathematical solutions will give us $[OH^-] = 4.5 \times 10^{-4}$, and $[OH^-] = 3.7 \times 10^{-7}$, and the corresponding pOH values will be 3.35 and 6.43. Since, as stated on p. 46, $p\text{H} + p\text{OH} = 14$ at 25°, the desired pH values will be $14 - 3.35 = 10.65$ and $14 - 6.43 = 7.57$.

Choice of Indicators in Titrations. The titration of an acid with a solution of a base is generally called a neutralization, but a sharp end point is obtained at $p\text{H} = 7$ only when the acid and base are both strong electrolytes. If the acid and base are equally strong, the end point with a weak acid and a weak base should occur at $p\text{H} = 7$ but it will not be sharp. This is illustrated by the plotted curves on p. 49. The titration of a weak acid with a weak base should be avoided whenever possible because of this difficulty in getting a sharp end point.

The curve on p. 49 for the titration of hydrochloric acid with sodium hydroxide shows that the titration is practically finished at about $p\text{H} = 3.5$ and the next drop of 0.1 N sodium hydroxide solution changes the pH to about 10.5. In reading such a curve, the true end point is taken as halfway up the nearly vertical line, which is at $p\text{H} = 7$ in this case. Any indicator that changes color between $p\text{H} = 3.5$ and $p\text{H} = 10.5$ should give a good result.

The curve for the titration of acetic acid with sodium hydroxide shows that the end point is at about $p\text{H} = 9$. Such a solution is alkaline because of the hydrolysis of sodium acetate. In this titration, therefore, the end point is not at the neutral point but at the *equivalence point, i.e.*, it occurs when a quantity of sodium hydroxide *equivalent* to the acetic acid present has been added. A study of the curve on p. 49 shows that methyl orange which changes color at $p\text{H} = 2.9$–4.0 is absolutely useless for this titration, but phenolphthalein which changes color at $p\text{H} = 8.3$–10 should give a good result. A similar study of the titration of ammonia with hydrochloric acid will show that phenolphthalein is useless and that methyl red or methyl orange can be used. From the ion product constant of water and the ionization constant of the weak acid or base to be titrated, it is possible to compute the pH value of the solution at the equivalence point, and when this is known the proper indicator can be chosen.

The hydrolysis of a salt can be expressed as follows:

$$BA + H_2O \rightleftarrows BOH + HA$$

when BA represents the formula of the salt, BOH that of the base, and HA that of the acid. Since most salts, excepting the halides of mercury and cadmium, are almost completely ionized in dilute aqueous solutions, this hydrolysis equation becomes

$$A^- + H_2O \rightleftarrows OH^- + HA \qquad (1)$$

when BOH is a strong electrolyte and HA is a weak acid. The mass-action law applied to this reaction of hydrolysis, and with the symbol K_h, is

$$\frac{[OH^-] \times [HA]}{[A^-]} = K_h \tag{2}$$

The quantity of water involved in the reaction is very small as compared with the total quantity of water in the solution so that $[H_2O]$ is regarded as a constant quantity and is left out of the mass-action law expression.

Now if we multiply equation 2 by $\frac{[H^+]}{[H^+]}$

$$\frac{[H^+] \times [OH^-] \times [HA]}{[H^+] \times [A^-]} = \frac{K_w}{K_a} = K_h \tag{3}$$

Now according to equation 1 equal quantities of OH^- and HA are formed by the hydrolysis so that in equation 2 we can replace [HA] with $[OH^-]$, and since the salt formed is practically completely ionized, we can replace $[A^-]$ with c, the concentration of the salt present in the solution. This gives us

$$\frac{[OH^-]^2}{c} = \frac{K_w}{K_a} = K_h \tag{4}$$

and

$$[OH^-] = \sqrt{\frac{K_w}{K_a} \cdot c}$$

Using logarithms we have

$$\begin{aligned} \log [OH^-] &= \tfrac{1}{2} \log K_w + \tfrac{1}{2} \log c - \tfrac{1}{2} \log K_a \\ &= -7 + \tfrac{1}{2} \log c + \tfrac{1}{2} p_a \end{aligned}$$

because $\log K_w = -14$ and $-\log K_a = p_a$.

Then, by changing all the signs, the equation becomes

$$-\log [OH^-] = pOH = 7 - \tfrac{1}{2} \log c - \tfrac{1}{2} p_a$$

and since, according to p. 46, $p\text{H} + p\text{OH} = 14$, and $p\text{H} = 14 - p\text{OH}$, the formula for computing pH at the equivalence point in titrating a *weak acid with a strong base* is

$$pH = 7 + \tfrac{1}{2} \log c + \tfrac{1}{2} p_a$$

Precisely the same line of reasoning leads us to the formula for the equivalence point in the titration of *a weak base with a strong acid*

$$pH = 7 - \tfrac{1}{2} \log c - \tfrac{1}{2} p_b$$

The values for p_a and p_b are given for a few acids on p. 62. These last two equations enable one to choose the proper indicator for the titration of a weak acid or a weak base of which the ionization constant is known.

The indicator chosen should change color at the pH indicated for the equivalence point.

It is sometimes possible to titrate a mixture of two acids in such a way that the quantity of each acid present is known. This is accomplished by using two indicators. With equal initial concentrations of the two acids it is possible to titrate each separately with an accuracy of less than 1 per cent if the ionization constants are to one another as 10,000:1, or, in other words, if the difference in the ionization constants is at least 10^{-4}. If there is 100 times as much of one as of the other, there must be a difference of 10^6 in the constants. Thus it is possible to titrate hydrochloric acid in the presence of boric acid or hydrochloric acid in the presence of acetic acid. In the same way it is possible to titrate carbonate in the presence of bicarbonate; the two ionization constants of carbonic acid are 4.9×10^{-7} and 6.3×10^{-11}, respectively. Phenolphthalein shows when the carbonate is converted into bicarbonate, and methyl orange shows when all the bicarbonate has reacted with a strong acid like hydrochloric. The ionization constants of phosphoric acid are $K_1 = 1.1 \times 10^{-2}$, $K_2 = 2.0 \times 10^{-7}$, and $K_3 = 3.6 \times 10^{-13}$. Methyl orange shows when the first end point is reached, and phenolphthalein indicates the second. An indicator changing at pH $12 - 14$ (trinitrobenzene) will give a fair idea of when the third hydrogen has all reacted, but the end point is not sharp.

Brönsted Definition of Acid and Base. Since the adoption of the ionization theory of Arrhenius in 1887, acids have been defined as substances which furnish hydrogen ions in aqueous solutions and bases as substances which yield hydroxide ions. In accordance with this conception, the neutralization of a dilute solution of acid by a base is expressed by the equation: $H^+ + OH^- \rightarrow H_2O$.

It has been known, for a long time, that the H^+ ions are not simply positively charged hydrogen atoms, or protons, but are hydrated just as most ions are. Under the Brönsted conception special emphasis is placed upon the fact that these hydrogen ions are hydrated; they are given the symbol H_3O^+ and called *hydronium* ions, *hydroxonium* ions, or *oxonium* ions by advocates of the system.

Brönsted's definition is based on the assumption that any substance can be considered as acid if it can lose a proton. A base is a substance which can accept a proton. Water acts as a base when it unites with a proton to form H_3O. When a compound behaves as an acid, it is transformed into its corresponding *conjugate base* as illustrated by the equation

$$\underset{\text{acid}}{A} \rightleftarrows \underset{\text{base}}{B^-} + \underset{\text{proton}}{H^+}$$

Since free protons are not present in solution, a dissolved acid will dissociate electrolytically only when the solvent can accept protons and act as a base. Just as water acts as a base to form H_3O^+ ions, so NH_4^+ ions dissolved in liquid ammonia have chemical properties which we regard as acidic.

In dealing with aqueous solutions, little is to be gained by the Brönsted formulation of acid-base equilibria with water. The mathematical treatment is essentially the same as when the Brönsted theory is not used. The chief points of difference are the substitution of *hydronium* ion for *hydrogen* ion and the change in the definition of acids and bases. Sodium carbonate is a salt in the older system, but the carbonate ion is a *base* according to Brönsted. We have always known, however, that the anions of compounds like Na_2CO_3 and $NaC_2H_3O_2$ have basic properties with respect to neutralizing acids, and Na_2CO_3 has been used to standardize solutions of acids ever since the early days of the nineteenth century. The Brönsted nomenclature is used by many modern writers who like to think of water, NH_3, $C_2H_3O_2^-$, CO_3^{--} as bases when they unite with H^+ ions to form H_3O, undissociated acetic acid, carbonic acid, etc. When, in this book, we speak of hydrogen ions and write the symbol H^+, we do so with the full realization that these ions are hydrated just as copper ions and most other ions are. The Brönsted terminology is somewhat more complicated than that of the older and more conventional system. A student brought up entirely on this newer nomenclature will be confused by many statements in current literature and in the older writings.

The titration of borax with hydrochloric acid can be used as an example of the different ways in which the underlying chemical reaction can be explained. Borax, according to the older nomenclature, is a salt of a strong base (NaOH) and a very weak acid (H_3BO_3). Borax dissolves in water but the acid is so weak that hydrolysis takes place to a considerable extent because boric acid is so weak that the $B_4O_7^{--}$ ions react with the H^+ ions of water to form H_3BO_3,

$$B_4O_7^{--} + 7H_2O \rightarrow 4H_3BO_3 + 2OH^-$$

and added H^+ ions react with the OH^- ions to form H_2O so that the final reaction results in the complete conversion of all $B_4O_7^{--}$ ions to H_3BO_3,

$$B_4O_7^{--} + 2H^+ + 5H_2O \rightarrow 4H_3BO_3$$

According to the Brönsted nomenclature, the $B_4O_7^{--}$ ion is what is called a *conjugate base* and reacts with H_3O^+ ions as follows:

$$B_4O_7^{--} + 2H_3O^+ + 3H_2O \rightarrow 4H_3BO_3$$

There is little to choose between the two explanations because the fundamental fact to be explained in both cases is that an aqueous solution of $Na_2B_4O_7$, with methyl red as indicator, can be titrated according to the equation

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3$$

LABORATORY EXERCISES

Preparation of 0.5 *N* Solutions of HCl and NaOH

To prepare 1 l of 0.5 *N* HCl, measure out approximately $0.5 \div 0.012 = 41.7$ ml of 12 *N* HCl or 83.3 ml of 6 *N* HCl and dilute to approximately 1 l. Since the solution is to be standardized, it is unnecessary to measure the acid or the water accurately. Pour the acid into an ordinary, glass-stoppered quart bottle, and fill with water up to about 2 in. from the bottom of the neck. It is important that enough empty space is left to permit thorough mixing by shaking. Stopper the bottle and shake for at least 2 minutes.

Prepare 1 l of 0.5 *N* sodium hydroxide by weighing out on the laboratory scales about 20 g of solid sodium hydroxide. Dilute with distilled water to about 1 l, and mix by shaking at least 2 minutes. Since this basic solution attacks glass slightly and sodium silicate is a good cementing agent, it is well to use a rubber stopper in the bottle and unwise to use the solution in a glass-stoppered buret.

Solutions of alkali hydroxide attack glass to form Na_2SiO_3. The reaction takes place slowly but becomes appreciable on standing. It is well to heat the empty bottle carefully to about 100° on the outside, place a piece of paraffin in it, and rotate until the inside of the bottle is thinly coated with paraffin. Solutions of acid also attack glass slightly on standing.

After the solutions are once mixed, the concentrations will remain uniform as a result of the osmotic pressure of the solutes, but there is always a slight loss by evaporation if the bottle is not kept stoppered. If a warm day is followed by a cool night there is likely to be some condensed moisture on the sides of the bottle so that is it always well to give the contents of the bottle a slight shaking every time a fresh portion is taken.

Take a plain buret that has been thoroughly cleaned with chromic acid solution (cf. p. 28) and washed with water. Never allow it to remain empty for any length of time; a buret that has been dry for some time will rarely drain well. When the buret is not in use, fill it with water, or with the solution which is used in it, and cap it with an inverted test tube. Rinse the buret with three 10-ml portions of the sodium hydroxide solution, emptying it each time. Discard the solution thus used. Fill the buret to slightly above the graduations, make sure that there is no entrapped air bubble in the rubber tubing at the bottom of the buret, which must be full of liquid, and then drain out the solution until the bottom of the meniscus at the upper level is exactly at 0.00 or slightly below. To remove entrapped air, bend the flexible tubing so that the tip points upward and allow a little solution to run out. In filling a buret, pour the reagent directly from the bottle into the buret. The use of a funnel or small beaker is likely to lead to error. In the same way, rinse out a carefully cleaned, glass-stoppered buret with water and with three separate portions of the 0.5 N acid, and fill to approximately the zero mark. Make sure that the bottom of the stopper is filled with liquid. Read each buret to the nearest 0.01 ml, and record the readings in the notebook (cf. p. 30 with respect to the use of blue, glazed paper). Measure out about 40 ml of the alkali hydroxide solution into a 200-ml Erlenmeyer flask, dilute with 50 ml of water, add 2 drops of methyl orange indicator solution and titrate with the acid until the solution *begins* to change from yellow to pink. As a rule a little too much acid will be added at first; if this happens, add a little more of the sodium hydroxide to turn the color back to a distinct yellow. Then add the acid very carefully until the well-stirred solution assumes a pink tint. Read each buret again.

Refill the burets and repeat the titration in the same way. Record the readings and compute the relative strengths according to the following scheme, which represents a sample page of a notebook.

TITRATION OF HCl *vs.* NaOH. OCT. 3, 1941

Determination	I	II
Final reading HCl	48.08	43.14
Initial reading HCl	0.12	0.17
	47.96	42.97
Final reading NaOH	46.29	40.37
Initial reading NaOH	1.75	0.50
	44.54	39.87
log ml HCl	1.6808	1.6332
log ml NaOH	1.6488	1.6007
	0.0320	0.0325*
1 ml of NaOH neutralizes	**1.076**	**1.077** ml HCl

* In titrations of one solution against another and in standardizations, the logarithms of the final values should agree within 0.0008. This corresponds to a check in the values of 2 parts in 1000. If necessary, repeat the work until this agreement is obtained.

The above procedure was made with a back titration. Sometimes it is advantageous to titrate to a *dead stop* end point. To do this in the titration of base with acid, keep the contents of the flask in constant motion, and, when a color change is apparent, close the buret and keep swirling the solution until the original yellow color is restored. Now add the acid more slowly, and, as the end point is approached, finally add the reagent dropwise, making sure that the yellow color is restored before adding a fresh drop. It is well to have for comparison a like volume of water containing the same quantity of indicator and a tiny drop of acid (0.02 ml) and end the titration when the two colors match. With a little practice, this *dead stop* end point can be determined as quickly and as accurately by this method as when a back titration is necessary because a slight excess of reagent was added.

Standardization of Acids and Bases

There are many excellent ways in which a solution of hydrochloric acid can be standardized with satisfactory accuracy. The standardization can be accomplished gravimetrically by taking a measured volume of the acid from a pipet or buret, diluting with water, adding a slight excess of silver nitrate, heating to coagulate the precipitate, filtering, and weighing the silver chloride precipitate. Such a procedure corresponds to the determination of chlorine in a sample of sodium chloride to be described later.

The acid solution can be standardized by measuring the volume required to react with a pure substance of definitely known chemical composition. A satisfactory standard is sodium carbonate prepared by heating pure sodium bicarbonate to 270°. Gay-Lussac recommended this method early in the nineteenth century. Other standards which have given good results are: calcite (Grandeau and also Pincus in 1863); potassium bicarbonate (Ure, 1839); sodium bicarbonate (North and Blakey, 1905); potassium bitartrate (Borntraeger, 1892), which is first converted into potassium carbonate by heating strongly; sodium oxalate (Sörenson, 1893), which is converted into sodium carbonate by ignition; and borax (Salzer and also Rimbach in 1893). Frequently it is convenient to standardize the acid against a solution or base which has itself been standardized. This last procedure is called the *indirect method.*

There is no good gravimetric method for standardizing a solution of sodium hydroxide, but numerous pure substances have been recommended as standards. Pure oxalic acid crystals, $H_2C_2O_4 \cdot 2H_2O$, were used by Fr. Mohr in 1852, and since then the following are only a few of the acids or acid salts which have been advocated: potassium acid oxalate, KHC_2O_4; potassium tetroxalate, $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$; succinic acid, $C_2H_4(CO_2H)_2$; potassium biiodate, $KH(IO_3)_2$; benzoic acid, $C_6H_5CO_2H$; potassium acid phthalate, $KHC_8H_4O_4$. An indirect method of standardizing sodium hydroxide solution is the titration against a solution of acid which has been standardized.

In this book two methods of standardizing the hydrochloric acid will be described in detail and three methods for standardizing the sodium hydroxide. The student may choose one of these and then determine the strength of his other solution indirectly, using the results that he has already obtained by titrating the hydrochloric acid against the sodium hydroxide.

Standardization of Acid against Sodium Carbonate, Na_2CO_3

Preparation of the Standard. If pure sodium bicarbonate is not available, dissolve about 35 g of the commercial product in 350 ml of warm water and filter off any insoluble residue. Allow the water to evaporate slowly at a temperature not above 40° until about 25 g of salt has deposited. Protect the solution from contamination by dust by covering it with a watch glass supported upon a glass triangle or glass supports. Finally pour off the mother liquor; dry the crystals by pressing them between filter papers and by heating for an hour at 120°. Preserve the pure sodium bicarbonate in a glass-stoppered bottle.

Place about 8 g of pure sodium bicarbonate in a platinum or porcelain crucible and heat for 30 minutes at a temperature of about 270°, taking care that the temperature does not rise above 300°. The heating can take place in an electric oven, a sand bath, or an air bath.

If a sand bath is used, embed the crucible so that the sand on the outside is level with the sodium bicarbonate on the inside. Occasionally stir the contents of the crucible with a 360° thermometer. After heating the crucible for half an hour, allow it and its contents to cool in a desiccator over calcium chloride or other suitable desiccant. Preserve the sodium carbonate in a glass-stoppered weighing bottle. If exposed to the air or kept in a cork-stoppered bottle it soon absorbs water from the atmosphere and becomes worthless as a standard.

Standardization. To standardize 0.5 *N* hydrochloric acid, weigh out two separate portions of about 1 g of sodium carbonate and record the weight to the nearest tenth of a milligram. The best way to do this is to place a little more than 2 g of the standard in a glass-stoppered weighing tube. Weigh this tube and its contents and record the weight after counting the missing places in the box of weights. Check this value by counting the weights on the pan. Every student is likely to make a mistake in recording a weight, but he will almost always notice the mistake if he habitually checks his observations. Take the weighed tube, remove the stopper, and pour out approximately the desired quantity of the sodium carbonate into an Erlenmeyer flask. Replace the stopper, and weigh again. If necessary, add more of the substance to the contents of the beaker.

A substance to be used in an analysis should never be weighed out on paper. If the substance is hygroscopic or deliquescent it should not be weighed on a watch glass. Many chemists are accustomed to weigh out ores on watch glasses, but the beginner will make fewer mistakes if he follows the procedure just outlined. For weighing samples of more than 0.5 g, metal weighing pans adjusted so that they weigh almost exactly 10.000 g can now be purchased and have proved satisfactory.

STANDARDIZATION OF HCl *vs.* Na_2CO_3

	I		II
Sample		12.4728	11.6484
		11.6778	10.9040
		0.7950	0.7444
HCl Last reading		33.34	33.77
First reading		0.02	0.03
		33.32	33.74
NaOH Last reading		0.14	2.66
First reading	1 ml NaOH	0.00	0.14
	= 1.076 ml HCl	0.14	2.52
ml NaOH × 1.076		0.15	2.71
Total HCl		33.32	33.74
Excess HCl		0.15	2.71
Net HCl		33.17	31.03
	m.e. Na_2CO_3		
	= 0.05300		
log sample		9.9004	9.8718
colog net HCl		8.4793	8.5082
colog 0.05300		1.2757	1.2757
		9.6554	9.6557
N HCl		0.4923 *N*	0.4926 *N*

A small spatula or palet knife should be used for transferring or removing the powder to the pan and a small camel's-hair brush is necessary to remove the last traces of powder from the pan to the flask. Record the data as indicated on page 71.

Dissolve the weighed portions of pure sodium carbonate in about 100 ml of distilled water, add one or two drops of methyl orange indicator solution, and titrate as described on pp. 68, 69.

Compute the concentration of the hydrochloric acid as indicated on p. 71, and from the value obtained compute the concentration of the sodium hydroxide solution as shown on p. 42. The equivalent weight of sodium carbonate is 53.00.

Gravimetric Standardization of Hydrochloric Acid

Measure out 10.00 ml of 0.5 *N* HCl with a tested pipet which has been cleaned with chromic acid mixture (p. 31) and rinsed with water and then three times with the 0.5 *N* HCl. In emptying the pipet into a 250-ml beaker, do not blow through it but touch it to the side of the beaker after the pipet has been emptied and a drop of liquid is left at the tip. Do not wait for a second drop to form. Dilute with about 100 ml of water, add 30 ml of 0.1 *N* $AgNO_3$, and heat carefully to gentle boiling. Stir occasionally, and continue heating with stirring until the AgCl precipitate coagulates, leaving a nearly clear supernatant solution. Filter and weigh as described for the gravimetric determination of chlorine in a chloride. (See Chapter X.)

Standardization of acid with borax has been recommended strongly. Most samples of borax are not sufficiently pure to use directly, and the $Na_2B_4O_7 \cdot 10H_2O$ is likely to effloresce into $Na_2B_4O_7 \cdot 5H_2O$. The sample must be recrystallized from water, preferably twice, and dried over deliquescent $NaBr \cdot 2H_2O$ in a desiccator. In this way a relative humidity of about 60 per cent prevails in the air above the borax. Borax has the advantage of a large equivalent weight (190.7 as compared with 53 for Na_2CO_3), and the titration is accurate. One molecule of borax reacts with two of HCl to a methyl red end point.

✓

$$Na_2B_4O_7 \cdot 10H_2O + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3$$

Sodium oxalate is another excellent standard. The weighed sample (equivalent weight 67) is heated very carefully over an alcohol flame, or in an electric oven at about 300°, until the $Na_2C_2O_4$ is converted into Na_2CO_3. It is not so important to keep the temperature below 270° as it is with $NaHCO_3$, for since the $Na_2C_2O_4$ was weighed, it makes no difference if a little Na_2O is formed which reacts with the same quantity of HCl as Na_2CO_3 does. The sample usually chars, but the deposited carbon does no harm.

An interesting method of standardizing acid is based on the reaction

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

The weighed sample of KIO_3 (equivalent weight 35.67) or $KH(IO_3)_2$ (equivalent weight 35.45) (in this case only), is dissolved in a solution which contains excess KI and sufficient $Na_2S_2O_3 \cdot 5H_2O$ to react with the liberated I_2:

$$2S_2O_3^{--} + I_2 = S_4O_6^{--} + 2I^-$$

The liberated iodine, therefore, does not color the solution, and, when all the iodate is decomposed, further addition of acid will cause the color change of an indicator such as methyl yellow, methyl orange, or bromocresol green.

Mercuric oxide, HgO (equivalent weight 108.3), has also been recommended. The weighed oxide is dissolved in an excess of KI solution, and the liberated OH^- is titrated with an acid in the presence of an indicator that changes color between *p*H 8 and 4.

$$HgO + 4I^- + H_2O \rightarrow HgI_4^{--} + 2OH^-$$

Standardization of Sodium Hydroxide

(*a*) *With Potassium Acid Phthalate, $KHC_8H_4O_4$*

This substance, because of its high molecular weight, is particularly well suited for the standardization of dilute solutions of sodium hydroxide. To standardize 0.1 *N* sodium hydroxide, about 1 g of the salt should be taken, as this is sufficient to neutralize 49 ml of the base. Phenolphthalein is a suitable indicator, but reliable results cannot be obtained with methyl orange. The chief difficulty that students have in working with phenolphthalein arises from the fact that the sodium hydroxide absorbs a little carbon dioxide from the air every time the storage bottle is opened, unless care is taken to prevent it. This can be accomplished by pumping the sodium hydroxide into the buret, or by siphoning it from the storage bottle, in such a way that all air that enters the bottle has to pass through a tube containing soda-lime ($Ca(OH)_2 + NaOH$) or Ascarite (a patented preparation of asbestos fibers impregnated with sodium hydroxide). Keeping the solution under a layer of gasoline is effective also. Every molecule of carbon dioxide that combines with two molecules of sodium hydroxide to form sodium carbonate yields a product that reacts only with one molecule of hydrogen chloride in the cold because the sodium bicarbonate, which is formed when one molecule of hydrochloric acid acts on one molecule sodium carbonate, is neutral to phenolphthalein. The resulting error can be overcome by boiling the acid solution to expel carbon dioxide and repeating the process if the phenolphthalein color of the neutralized solution is discharged by heating. If the ratio of acid to base has been determined with methyl orange as indicator, the presence of carbonate in the sodium will be detected by determining the ratio with phenolphthalein as indicator. The sodium hydroxide solution will prove weaker when phenolphthalein is used if it contains carbonate and the titration is carried out in the cold.

Procedure. To standardize 0.5 *N* sodium hydroxide, weigh out 2.5- to 3.0-g portions of potassium acid phthallate into 200-ml Erlenmeyer flasks. Record the weights to the nearest milligram. Add 100 ml of water to each portion and shake gently until all the solid has dissolved. Add 3 drops of phenolphthalein solution and titrate till a pale pink color is obtained. Heat the solution to boiling; if the color fades, add more of the sodium hydroxide solution until the color persists after boiling for 30 seconds. Record the data as shown on p. 71. The equivalent weight of potassium acid phthalate is the molecular weight, 204.1. Compute the normal concentration of the base, and, from the ratio of acid to base previously found, compute the normal concentration of the hydrochloric acid solution as well.

For the most accurate work, the solution of sodium hydroxide must be prepared free from carbonate, the water used for dissolving the standard must have been recently boiled to remove carbon dioxide, the titration must take place in a flask which has been swept free from carbon dioxide by passing through it a stream of air that has been made to flow through granular soda-lime or Ascarite, and a blank test must be run under the same conditions to see how much sodium hydroxide would have been used if no potassium acid phthalate had been present. The volume used in the blank test must be deducted from that used in the standardization.

(b) *With Benzoic Acid*

Weigh out 1.5- to 2.0-g portions of the pure acid into 200-ml flasks, and record the weights to the nearest milligram. Add 40 ml of alcohol, stopper the flask, and allow to stand until all the acid has dissolved. Add 3 drops of phenolphthalein indicator, dilute with water to 100 ml, and titrate with the 0.5 N sodium hydroxide. When a slight pink color is obtained, heat the solution and see if the color disappears. If so, add more sodium hydroxide until the color is not bleached by boiling for 30 seconds. Run a blank test with the same quantities of water and alcohol, and deduct the volume of sodium hydroxide required in this test from the total volume used in the standardization.

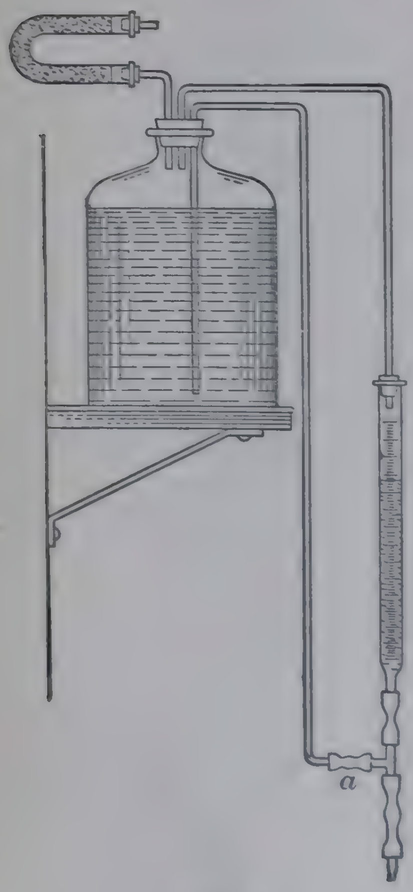

FIG. 6.

Everything that was said under (a) concerning the effect of carbon dioxide is true here. Sodium hydroxide free from carbonate can be prepared by adding about 20 ml of 0.5 N barium chloride to the sodium hydroxide solution. Allow the precipitate of barium carbonate to settle; stopper the bottle with a two-hole rubber stopper carrying a short right-angled tube attached to a soda-lime tube through which air can enter the bottle and also carrying a siphon tube reaching nearly to the bottom of the bottle. Then place the bottle on a shelf above the buret and siphon the solution into the buret as required. See Fig. 6. The valve at *a* is made by a round bead in the rubber tubing.

(c) *With Constant-Boiling Hydrochloric Acid*

Set up a distilling apparatus with a liter flask and a water-cooled condenser. Place in the flask about 750 ml of approximately 6 *N* HCl and distil at the rate of 3–4 ml per minute. After about three-quarters of the original liquid has been distilled and rejected, collect the constant-boiling acid in a dry flask. Continue distilling until only 50–60 ml of liquid remains in the distilling flask. Preserve in a glass-stoppered bottle. Read the barometer to the nearest millimeter. The exact composition of the liquid varies slightly with the barometric pressure that prevails during the distillation, as the following table shows.

ATMOSPHERIC PRESSURE IN MILLIMETERS OF MERCURY	WEIGHT OF HCl IN 1 g OF DISTILLATE
780	0.2018
770	0.2020
760	0.2022
750	0.2026
740	0.2027
730	0.2030

Each millimeter difference in barometric pressure corresponds to about 0.02 mg in the actual HCl content of 1 g of the acid. The value for any intermediate pressure can be interpolated with an accuracy of 1 part per 1000 or better.

To use the acid for standardizing 0.5 *N* NaOH, weigh a clean and dry glass-stoppered weighing tube to the nearest 0.1 mg, add 3–4 ml of the constant-boiling acid, weigh the tube again, and transfer to a 200-ml Erlenmeyer flask by washing the tube thoroughly with a stream of water from a wash bottle. Dilute to about 100 ml, add methyl red or methyl orange indicator solution, and titrate to the color change.

The acid can also be weighed from a weight buret such as that shown in Fig. 7, p. 78. It can be used for preparing standard solutions by diluting a weighed portion to the mark in a volumetric flask and mixing.

Analysis of Soda Ash

Soda ash is the trade name for anhydrous sodium carbonate. The following procedure is applicable to the analysis of any alkali carbonate. It can also be used for an alkaline-earth carbonate but then it is necessary to add an excess of acid and titrate back with sodium hydroxide solution. As we have seen in the discussion of indicators, carbonic acid is such a weak acid that it has practically no effect upon methyl orange. The primary ionization of carbonic acid, however, furnishes hydrogen ions sufficient to make phenolphthalein assume its colorless form. With methyl orange as indicator, sodium carbonate Na_2CO_3 can be titrated as if it were two molecules of sodium hydroxide, both stages of the following decomposition taking place before the solution is acid to methyl orange:

$$CO_3^{--} + H^+ \rightarrow HCO_3^-$$
$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$

With phenolphthalein in the cold, an end point is obtained when the first stage only has taken place.

With an insoluble alkaline-earth carbonate, on the other hand, the carbonate does not begin to dissolve until the solution is more acid than corresponds to the phenolphthalein end point, so that a mixture of soluble $Ba(OH)_2$ and insoluble $BaCO_3$ can be titrated with acid and an end point obtained as soon as the $Ba(OH)_2$ has been completely neutralized provided that phenolphthalein is the indicator. With methyl orange, on the other hand, a permanent end point will not be reached until all the insoluble carbonate has dissolved.

Procedure. Weigh out into 250-ml Erlenmeyer flasks, two samples of about 1 g each. Record the weights to four significant figures.[1] Fill a glass-stoppered buret with standardized hydrochloric acid and a plain buret with standardized sodium hydroxide. Record the initial readings in the notebook to the nearest 0.01 ml.

Cover the sample with 25 ml of water and add 2 drops of methyl orange indicator solution. Run in acid slowly until the indicator turns distinctly red, rotating the contents of the flask. With an insoluble carbonate, it will be necessary to add a few milliliters of excess acid. When all the carbonate is decomposed, wash down the sides of the flask and carefully add sodium hydroxide from the buret while keeping the liquid in the flask in motion. Stop adding the hydroxide as soon as the liquid becomes distinctly yellow. Finally add acid dropwise until the well-mixed solution shows a faint change toward the pink. In order to determine the end point accurately, the beginner should have two comparison solutions both containing the same amount of indicator as used in the analysis and approximately the same volume as at the end of the titration. For one solution have the indicator in distilled water; the color will be yellow, because water reacts basic to methyl orange. For the other comparison solution, add a drop of the standardized acid, or just enough to change the methyl orange color toward the pink. This shade should be matched in the titration.[2]

From the total volume of hydrochloric acid used, deduct the volume of hydrochloric acid corresponding to the sodium hydroxide added, and

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[1] See p. 20, regarding significant figures. In general, no more significant figures should be used in analyses than the accuracy of the result warrants. In reporting results, the next to the last figure kept should not vary by more than two units.

[2] It is also well to have as much neutral sodium chloride present as will be formed by the titration.

ANALYSIS OF A CARBONATE. NO. 3652. OCT. 8, 1941

	I	II
Sample	15.3620	14.4875
	14.4875	13.5020
	0.8745	0.9855
HCl (0.4525 *N*)	37.36	41.55
	0.04	0.02
	37.32	41.53
NaOH (0.4870 *N*)	1.12	1.80
	0.02	1.12
	1.10	0.68
	$1.10 \times \frac{0.4870}{0.4525} = 1.18$	$0.68 \times \frac{0.4870}{0.4525} = 0.73$
Total HCl	37.32	41.53
Excess HCl	1.18	0.73
Net HCl	36.14	40.80
log ml HCl	1.5580	1.6107
log *N* HCl	9.6556	9.6556
log m. e. Na_2CO_3	8.7243	8.7243
colog sample	0.0583	0.0064
	9.9962	9.9970
Per cent Na_2CO_3	99.13%	99.31%

this will give the volume of hydrochloric acid actually required to react with the weight of the carbonate used. Record and compute the analysis as shown above. The milliequivalent weight of Na_2CO_3 in this determination is the molecular weight divided by 2000; the same is true of Na_2O.

Analysis of Oxalic Acid

Assume that the sample given you is oxalic acid,[1] $H_2C_2O_4 \cdot 2H_2O$, and report the results in terms of this acid, the equivalent weight of which is 63.02. Record the results in the notebook according to the method shown for the preceding analysis. Remember that the net milliliters of sodium hydroxide is required in this analysis and that the value of 1 ml of HCl solution in terms of NaOH solution is the reciprocal of the value of 1 ml NaOH solution in terms of HCl.

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[1] Potassium binoxalate, potassium tetroxalate, benzoic acid, and potassium acid phthalate are other suitable substances to use for this analysis. Students find it more interesting not to know exactly what they are analyzing.

Procedure. Weigh out portions of the sample of about 1.25 g each to the nearest milligram, dissolve in 50 ml of hot water, add 2 drops of phenolphthalein solution, and titrate till the solution is pink. If the sodium hydroxide contains much carbonate, shown by effervescence when the reagent is added to the oxalic acid solution, make the solution slightly acid with standardized hydrochloric acid added from the buret (0.5 ml), boil gently for 1 minute, and finish the titration after cooling under the cold water tap. Allow for the hydrochloric acid added.

Remark. To avoid errors in reading burets, chemists often prefer to weigh the solution used for titrating with the aid of a weight buret. Figure 7 shows such a buret.[1] If the weighings are corrected for air displacement, the accuracy of the work is increased so that the error in determining the end point is the chief one to be considered.

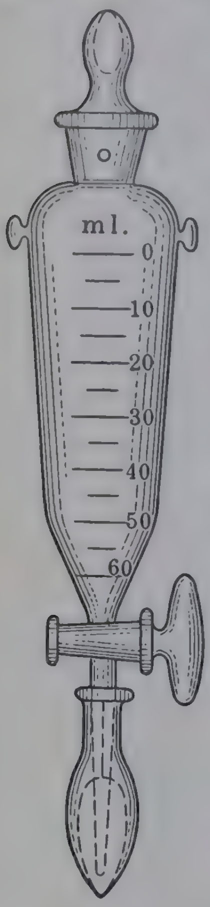

FIG. 7.

Determination of Total Acid in Vinegar

Weigh a glass-stoppered weighing tube to the nearest milligram. Add to it about 5 ml of vinegar, and reweigh. Transfer to a 200-ml Erlenmeyer flask, and dilute with cooled, boiled water until the color of the solution is not enough to interfere with a phenolphthalein end point. Add phenolphthalein indicator, and titrate with 0.5 N NaOH which is free from carbonate (see p. 74). Analyze three separate portions; the average deviation should not exceed 2 parts per 1000. Report the percentage of acetic acid (equivalent weight 60.05), and assume that this is the only acid present.

Concentrated Acids

Determination of the Acid Content of Oleum (Fuming Sulfuric Acid)

Highly concentrated acids must be always weighed and not measured volumetrically, in order to avoid loss by evaporation. The weighing is best accomplished by means of the Lunge-Rey pipet, shown in Fig. 8, but a glass-stoppered weighing tube can be used as in the analysis of vinegar.

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[1] Friedman and La Mer, *Ind. Eng. Chem., Anal. Ed.*, **2**, 54 (1930).

Remove the lower tube, introduce 0.5 ml of water, and weigh together with the dry upper pipet, but leaving the two parts unconnected. Close the lower stopcock, open the upper one, and produce a slight vacuum in the bulb by sucking through the upper tube and then closing the stopcock. Dip the dry point of the pipet into the fuming acid (if it is of solid pyrosulfuric acid, first melt it by warming slightly), and open the lower stopcock. As soon as the widened part of the pipet below the lower bulb is one-half to three-fourths full, close the stopcock, taking care that none of the liquid reaches up to it.

Carefully wipe off the acid on the outside of the pipet with filter paper; connect the two parts of the pipet and again weigh. The quantity of acid taken for the analysis should amount to 0.5–1 g. Dip the point of the pipet into about 100 ml of distilled water contained in a beaker, and, by opening first the upper stopcock and then the lower, allow the acid to run into the water. Rinse out the pipet, add the rinsings to the contents of beaker, add methyl orange, and titrate with 0.5 N sodium hydroxide.

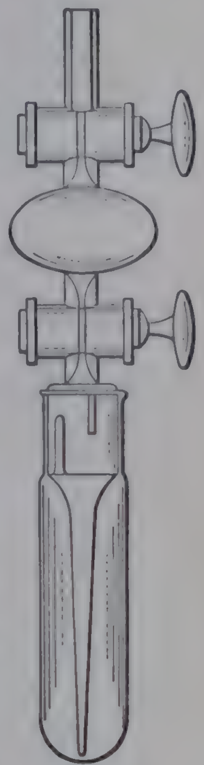

FIG. 8.

Computation. Fuming sulfuric acid can be considered to be a solution of anhydrous SO_3 in H_2SO_4.[1] On treatment with water, the following reaction takes place: $SO_3 + H_2O = H_2SO_4$. The titration with NaOH, therefore, shows the total acid present, including that formed from the anhydride. Let p be the weight of the original sample and n the milliliter of N-normal NaOH used. The total weight of H_2SO_4 (equivalent weight 49) in the solution after the reaction with water is

$$n \times N \times 0.049 = p_2$$

Then $p_2 - p$ is the weight of the water which reacted with the anhydrous SO_3. Since 1 mole of H_2O (18.02 g) reacts with 1 mole of SO_3 (80.06 g), evidently 1 g of H_2O reacts with $80.06 \div 18.02 = 4.443$ g of SO_3 and $p_2 - p$ grams of water are equivalent to $4.443\ (p_2 - p)$ grams of anhydrous SO_3. This value subtracted from the weight, p, gives the original weight of H_2SO_4.[2]

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[1] Fuming sulfuric acid contains a little SO_2 but as its determination involves an iodimetric titration it will not be considered here. The analysis of fuming sulfuric acid is not a suitable exercise for beginners, but the method is described because the calculation should be understood.

[2] This value $80.06 \div 18.02$, or SO_3/H_2O, where each formula represents a molecular weight, is what is called a *chemical factor*. It represents the weight of SO_3 corresponding to a unit weight of H_2O so that, if the weight of water is known, the corresponding weight of SO_3 is obtained by multiplying the weight of water by this chemical factor. The chemical factor represents the weight ratio of weight desired ÷ weight obtained, but it is necessary always to use equivalent quantities in such chemical factors. Thus if 1 molecule of H_2O reacted with 2 molecules of SO_3, the chemical factor would be $H_2O/2SO_3$.

A similar computation applies to the analysis of a mixture of acetic acid and acetic anhydride. When treated with water the latter reacts as follows: $(CH_3CO)_2O + H_2O = 2CH_3CO_2H$ (acetic acid). The result of the NaOH titration, expressed in terms of acetic acid, will give a weight larger than that of the original sample, the excess representing the weight of water that reacted with the anhydride; and the chemical factor for converting this weight of water into the equivalent weight of the anhydride is

$$\frac{(CH_3CO)_2O}{H_2O} = \frac{72.05}{18.02} = 3.998$$

Titration with Two Indicators

Determination of Alkali Carbonate in the Presence of Either Alkali Hydroxide or Alkali Bicarbonate

If a solution of sodium hydroxide is titrated with tenth-normal hydrochloric acid, the reaction is practically complete at about $pH = 11$. When sodium carbonate, Na_2CO_3, is titrated with tenth-normal hydrochloric acid, it is completely changed to $NaHCO_3$ at about $pH = 10$ and the sodium bicarbonate is changed to chloride at about $pH = 4$. It happens, fortunately, that the color change with phenolphthalein takes place after the sodium hydroxide has been completely neutralized and just after the carbonate has been converted to bicarbonate. Methyl orange, on the other hand, does not show an acid reaction until the sodium bicarbonate is changed completely to sodium chloride.

$$\left.\begin{array}{r}OH^- + H^+ \rightarrow H_2O \\ CO_3^{--} + H^+ \rightarrow HCO_3^-\end{array}\right\}\text{end point with phenolphthalein}$$
$$HCO_3^- + H^+ \rightarrow H_2O + CO_2 \uparrow \quad \text{additional reaction with methyl orange}$$

In carrying out the analysis it is important to make sure that there is no loss of CO_2 before the first end point is reached; the solution must be cold, the acid must be added slowly, and each portion must be stirred in well before fresh acid is added.

Procedure. Weigh out 5 g of the sample to four significant figures, dissolve in water, and make up to exactly 500 ml in a measuring flask. Mix well by pouring back and forth into a beaker at least four times, and take 25-ml portions of the solution with a pipet for the further analysis.

To one portion, add some phenolphthalein indicator, chill by placing the flask in ice water, and titrate slowly with $0.1\ N$ hydrochloric acid while stirring constantly. Titrate to match the rose color obtained by adding phenolphthalein indicator to a solution of approximately the same concentration of pure sodium bicarbonate. Let T_1 represent the milliliters of acid required to decolorize the solution.

To another portion add methyl orange and titrate till the color of the solution begins to change from yellow to pink. Let T_2 represent the total milliliters of acid used to make the solution acid to methyl orange.

Computation. (*a*) If T_2 is more than twice as large as T_1, the original sample is a mixture of carbonate and bicarbonate. (*b*) If T_2 is less than twice as large as T_1 the sample contains carbonate and hydroxide.

(*a*) Now n moles of CO_3^{--} react with n moles of H^+ in the phenolphthalein titration and with 2 n moles of H^+ in the methyl orange titration; m moles of HCO_3^- react with no acid in the first titration and with m moles of H^+ in the second titration. In a mixture of n moles of CO_3^{--} and m moles of HCO_3^-, when T_1 ml of N-normal HCl is used in the phenolphthalein titration and T_2 ml of acid in the methyl orange titration:

$$T_1 \times N = n = \text{number of millimoles of } CO_3^{--}$$

$$(T_2 - 2T_1)N = m = \text{number of millimoles of } HCO_3^-$$

(*b*) If T_2 is less than twice as large as T_1, the original sample is a mixture of alkali hydroxide and carbonate

$$(T_2 - T_1)N = \text{number of millimoles of } CO_3^{--}$$

$$(2T_1 - T_2) \times N = \text{number of millimoles of } OH^-$$

Note. This method of analysis, which applies to the analysis of alkali carbonate, hydroxide, and bicarbonate mixtures but not to mixtures of alkaline-earth carbonate with hydroxide and bicarbonate, is not so satisfactory as Winkler's method which depends upon the titration of one sample with methyl orange as indicator and of another sample with phenolphthalein as indicator after treatment with barium chloride, which precipitates barium carbonate. A solution containing *soluble* alkali or alkaline-earth hydroxide in the presence of *insoluble* alkaline-earth carbonate can be titrated with acid and the phenolphthalein end point obtained as soon as the hydroxide has been neutralized completely and before any of the insoluble carbonate dissolves. With methyl orange, however, the end point is not reached until all the alkaline-earth carbonate has dissolved. The carbonate dissolves very slowly toward the last; it is best, therefore, to add an excess of acid and, then, when all the alkaline-earth carbonate is dissolved, titrate back to a methyl orange end point.

Analysis of Phosphate Mixtures

The three ionization constants of phosphoric acid are $K_1 = 1.1 \times 10^{-2}$, $K_2 = 1.95 \times 10^{-7}$, and $K_3 = 3.6 \times 10^{-13}$. The first hydrogen can be titrated fairly accurately with methyl orange as indicator, and the first two hydrogens can be titrated with phenolphthalein as indicator. The third hydrogen is ionizable to such a slight extent that it cannot be titrated accurately. In other words, phosphoric acid, H_3PO_4, has 1 replaceable hydrogen when methyl orange is the indicator and 2 replaceable hydrogen atoms when phenolphthalein is the indicator. Monosodium phosphate, $NaH_2PO_4 \cdot H_2O$, is neutral to methyl orange but has 1 replaceable hydrogen when phenolphthalein is the indicator. Disodium phosphate, $Na_2HPO_4 \cdot 12H_2O$, is neutral to phenolphthalein but requires 1 mole of acid to make it neutral to methyl orange. Trisodium phosphate is alkaline to both indicators but requires 2 moles of acid to make it neutral to methyl orange and only 1 mole to make it neutral to phenolphthalein.

To illustrate the extent to which titrations of separate portions of the same solution to the methyl orange and phenolphthalein end points can aid in the interpretation of the results of chemical analysis, let us assume that qualitative tests show the presence of only Na^+, Cl^-, and PO_4^{---}, and that we are dependent upon the results of titrations with the above two indicators to determine which of the following substances are present — HCl, H_3PO_4, NaH_2PO_4, Na_2HPO_4, Na_3PO_4, and NaOH. The analytical procedure would be something like this:

Make the solution up to a definite volume in a measuring flask. Mix thoroughly, and take suitable aliquots of the diluted solution. To one portion add a little methyl orange indicator and titrate to a color like that shown by the same quantity of indicator in the same volume of 0.1 *M* NaH_2PO_4 solution. To another aliquot portion add phenolphthalein indicator and titrate to a colorless end point if the original solution is basic, or to a pale pink if the original solution is acidic.

There are no less than nine different possibilities. In four cases the solution will be acid to both methyl orange and phenolphthalein; in four others the solution will be alkaline to both indicators. In one mixture the solution will be alkaline to methyl orange and acid to phenolphthalein. It is impossible to determine the NaCl content of the solution by these titrations, but, of the substances listed above, any one can be present alone and we can have a mixture of any two neighboring compounds as listed. We can assume that HCl reacts with Na_2HPO_4 to give H_3PO_4, H_3PO_4 reacts with Na_2HPO_4 to give NaH_2PO_4, and NaH_2PO_4 reacts with Na_3PO_4 to give Na_2HPO_4. Although these reactions may not go *absolutely* to completion, the differences in the three ionization constants show that we do not incur serious error in making the above assumptions. In other words, the results ought to be good to within about 1 per cent of the truth.

Computation. *A. The solution is acid to both indicators.* Let T_1 represent the milliliters of N_b-normal sodium hydroxide required in the methyl orange titration and T_2 the milliliters of N_b-normal sodium hydroxide required in the phenolphthalein titration. The relative values of T_1 and T_2 can vary in four ways:

(*a*) $T_2 = T_1$. The solution contains hydrochloric acid alone. This is contrary to the fact that the presence of a soluble phosphate was shown by qualitative analysis.

(*b*) $T_2 > T_1$ but $T_2 < 2T_1$. The solution contains hydrochloric acid and phosphoric acid. $(T_2 - T_1)N_b$ millimoles of H_3PO_4 are present and $(2T_1 - T_2)N_b$ millimoles of HCl.

(*c*) $T_2 = 2T_1$. The solution contains $T_1 \cdot N_b$ millimoles of H_3PO_4.

(*d*) $T_2 > 2T_1$. The solution contains $T_1 \cdot N_b$ millimoles of H_3PO_4 and $(T_2 - 2T_1)N_b$ millimoles of NaH_2PO_4.

B. The solution is neutral to methyl orange and acid to phenolphthalein. The volume of NaOH used is a direct measure of the NaH_2PO_4 and no other acid or basic constituent is present.

C. The solution is basic to methyl orange and acid to phenolphthalein. A mixture of Na_2HPO_4 and NaH_2PO_4 is present.

D. The solution is basic to methyl orange and neutral to phenolphthalein. The volume of acid used in the methyl orange titration is a direct measure of the Na_2HPO_4 of which 1 millimole = 1 milliequivalent.

E. The solution is basic to both methyl orange and phenolphthalein. Let T_1 represent the milliliters of N_a-normal HCl used in the methyl orange titration and T_2 the milliliters used with phenolphthalein. As under *A* there are four different cases depending upon the relative volumes used in the two titrations.

(*a*) $T_1 > 2T_2$. The solution contains $(T_1 - 2T_2)N_a$ millimoles of Na_2HPO_4 and $T_2 \cdot N_a$ millimoles of Na_3PO_4.

(*b*) $T_1 = 2T_2$. The solution contains $T_2 \cdot N_a$ millimoles of Na_3PO_4.

(*c*) $T_1 < 2T_2$ but $T_1 > T_2$. The solution contains $(T_1 - T_2)N_a$ millimoles of Na_3PO_4 and $(2T_2 - T_1)N_a$ millimoles of NaOH.

(*d*) $T_1 = T_2$. Only NaOH is present. This, like *A* (*a*), is contrary to the assumption that phosphate is present.

Kjeldahl Method for Determining Nitrogen

The Kjeldahl method for determining nitrogen in organic substances consists in converting the nitrogen into ammonium acid sulfate while decomposing the organic matter with boiling sulfuric acid and some catalyzer. For student work when the class is large, a sample of blood meal mixed with flour is suitable for this analysis.

After the organic matter has been decomposed completely, the solution is made alkaline with sodium hydroxide, liberating ammonia which is distilled into a measured volume of standardized acid solution or into boric acid solution. The excess of the standardized acid is finally titrated with standard sodium hydroxide with methyl red as an indicator or the ammonium borate is titrated directly with standard acid (cf. p. 85). One milliliter of normal acid neutralizes 0.014 g of nitrogen in the form of ammonia.

The method has undergone much modification from time to time in order to include in the results nitrogen which is not easily reduced to ammonia. Thus to include nitrogen present as nitrate it is customary to add 0.04 g of salicylic acid for each milliliter of concentrated sulfuric acid used.

To test for nitrate in the presence of organic matter, heat a little of the sample with 10 ml of water. Place 1 ml of concentrated sulfuric acid in a porcelain crucible and dissolve in it 2–3 mg of carbazole (diphenylimide, $C_6H_5 \cdot NH \cdot C_6H_5$). Add, with stirring, a little of the aqueous solution to be tested for nitrate; a deep green color shows the presence of nitrate (disregard a slight coloration). If nitrate is present, digest the sample with 30 ml of concentrated sulfuric acid containing 1 g of salicylic acid. Mix by shaking, and allow to stand 30 minutes. Then add in small portions 5 g of powdered $Na_2S_2O_3 \cdot 5H_2O$ and heat 5 minutes. Cool under running water, add the catalyzers, and continue as in the absence of nitrate.

Procedure. Weigh out 0.35 to 3.5 g of finely ground substance into a 500-ml Kjeldahl flask,[1] add 10 g of powdered potassium sulfate, 0.2 g selenium, and 20 to 25 ml of concentrated sulfuric acid. Shake to mix the contents of the flask; place over a hole in an asbestos board on the ring of a lamp stand with the flask inclined at an angle of about 60°. Heat below the boiling point until there is no more frothing, adding a little paraffin wax if the frothing is violent. Take care to use a small flame protected by the asbestos board so that the flame does not touch the flask except where the inside is wet with acid. Gradually increase the heat until the decomposition is complete and the solution is nearly colorless. Boil gently for about 30 minutes, allow to cool, and connect with another flask, and a condenser through splash trap as shown in Fig. 9. The flask on the right contains water from which steam is generated. When heated in this way the solution in the other flask can be boiled without bumping. The side-armed distilling flask shown between the flask and the condenser acts as an efficient splash trap and prevents any spray containing NaOH from being carried over mechanically into the receiver. In the receiver (a 250-ml Erlenmeyer flask) place 50 ml of 5 per cent boric acid solution. Dilute the H_2SO_4 solution with about 200 ml of water, poured through the funnel of the flask, and add sufficient 12 *N* NaOH to make the solution basic (80 ml should be sufficient). Distil over about 150 ml of liquid by boiling the water in the flask shown on the right. This boiler should have a safety tube extending from the bottom of the flask to at least a foot above the neck. The boric acid in the receiver helps to retain the NH_3, but the acid is so weak that the ammonium borate formed titrates exactly as if it were free ammonia. After the distillation, remove the receiver, wash down the condenser tube, add the washings to the contents of the receiver, and titrate with standard HCl solution to a methyl red or better bromocresol red end point. The equivalent weight of N = 14. $NH_3 + H^+ \rightarrow NH_4^+$ or

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[1] Kjeldahl flasks can be obtained which are suitable both for the original digestion with the acid and for the subsequent distillation. If a smaller Kjeldahl digestion flask is used, rinse the solution into a larger flask before adding the sodium hydroxide to make the solution alkaline.

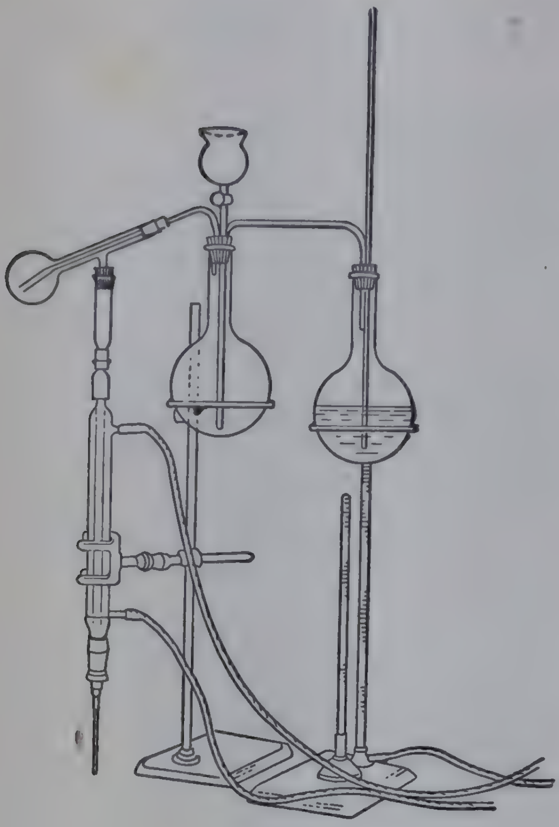

FIG. 9.

$$(NH_4)_2B_4O_7 + 2H^+ + 5H_2O \rightarrow 2NH_4^+ + 4H_3BO_3$$

Analysis of Borax

Although commercial borax is cheap, the carefully purified product is costlier and has been adulterated sometimes with cheaper substances like sodium bicarbonate. The presence of such an adulterant is easily detected by the effervescence that takes place when the sample is treated with acid. Some of the detergents sold commercially contain borax together with other substances of basic reaction such as sodium carbonate. The methods described for the analysis of alkaline carbonates and for phosphate mixtures can be applied with slight modification to the examination of mixtures containing borax.

Boric acid is a very weak acid. Its primary ionization constant, 6.0×10^{-10}, is almost as small as the secondary ionization constant of carbonic acid. A solution of borax in water, therefore, reacts with the same quantity of hydrochloric acid when methyl red or methyl orange is the indicator as if the sodium of the $Na_2B_4O_7$ were present as NaOH. Pure, recrystallized borax, therefore, of the formula $Na_2B_4O_7 \cdot 10H_2O$, has been recommended as a primary standard in acidimetry.

Although boric acid itself is so weak that it requires an indicator changing at $pH = 11$ (tropeolin 0 or nitramine) to determine the end point when a molar solution is titrated with one equivalent of sodium hydroxide, the acid has the peculiar property of forming complexes with polyhydric alcohols which have a much larger ionization constant than boric acid itself. Thus if the aqueous solution of borax is neutralized to an end point with methyl orange and there is then added to the solution some glycerol, mannitol, invert sugar, or dextrose, the solution can be titrated with sodium hydroxide to an end point with phenolphthalein at $pH = 8 - 9$.

Procedure. Weigh out carefully about 1.0 g of the sample, add 50 ml of 0.5 *N* hydrochloric acid, and heat to 80°. Filter if any insoluble residue remains, and wash the filter with hot water until the liquid that runs through the filter does not turn blue litmus red. Add 2 drops of methyl orange indicator, and titrate with 0.5 *N* sodium hydroxide until the mixture has a clear lemon-yellow color.

Now add 3 drops of phenolphthalein indicator solution and about 1 g of mannitol. Titrate with 0.5 *N* sodium hydroxide to a permanent pink color. Add 0.5 g more of mannitol, and, if the color fades, add more sodium hydroxide. Instead of mannitol, 50 ml of glycerol can be used followed by 10-ml portions until the color ceases to fade.

If the sample contained no basic substance other than borax, the volume of 0.5 *N* hydrochloric acid required to react with it to a methyl orange end point should be one-half that of the 0.5 *N* sodium hydroxide required in the final titration.

Equivalent weight of $Na_2B_4O_7 \cdot 10H_2O = 190.7$ against hydrochloric acid with methyl orange or methyl red as indicator and 95.35 against sodium hydroxide after neutralization to methyl orange and introduction of mannitol.

HOME PROBLEMS

21. A sample of soda ash weighing 1.682 g was analyzed by the method described on p. 75. In the analysis 48.6 ml of HCl solution were used and 2.32 ml of NaOH solution. One milliliter of HCl = 0.9852 ml of NaOH. One milliliter of NaOH = 0.1325 g of pure $KHC_8H_4O_4$. Compute the total alkaline strength of the soda ash in terms of Na_2O and also in terms of Na_2CO_3.

22. What weight of soda ash should be taken for analysis, with methyl orange as indicator, such that the milliliters of 0.55 *N* HCl needed will be numerically the same as (*a*) the percentage of Na_2CO_3 present; (*b*) the percentage of Na_2O present. (This last method of expressing the result is based on the old dualistic formula of sodium carbonate, $Na_2O \cdot CO_2$.)

23. A mixture of $BaCO_3$ and Li_2CO_3 weighing 1.25 g requires 41.67 ml of 0.600 *N* HCl to convert it into water-soluble chlorides. Find the percentage of BaO, Li_2O, and CO_2 in the mixture. (*Hint.* The acid titration gives the total number of milliequivalents of carbonate. Assume that x milliequivalents of one of the carbonates is present. The problem can also be solved by assuming that x g of one of the carbonates is present but the solution is then a little longer.)

24. Calculate the percentage of $H_2C_2O_4 \cdot 2H_2O$ in a sample of which 1.260 g was titrated with 45.77 ml of 0.460 *N* NaOH and 2.10 ml of HCl. One milliliter of HCl neutralizes 0.0265 g of pure Na_2CO_3.

25. In the Kjeldahl method of determining nitrogen, this element is eventually obtained as NH_4HSO_4, which is heated with strong caustic alkali and the liberated ammonia can be distilled off and collected in a measured volume of standard acid, the excess of which is finally titrated. Compute the percentage of N in a substance from the following data: weight of sample, 5.0 g; used 90 ml of 0.5 *N* H_2SO_4 to absorb the ammonia; excess acid reacted with 22.0 ml of 0.1 *N* NaOH.

26. If the ionization constant of acetic acid is 1.8×10^{-5}, compute the *p*H value of a liter (*a*) of water containing the equivalent of 6 ml of normal acetic acid and (*b*) of another solution containing the same quantity of acetic acid and 4.1 g of $NaC_2H_3O_2 \cdot 3H_2O$.

27. Find the *p*H of 0.05 *N* HCl solution on the assumption that the ionization of the acid is 90 per cent.

28. What indicator could be used for the titration of (*a*) vinegar with 0.25 *N* NaOH, (*b*) ammonia solution with 0.25 *N* HCl? Assume 40 ml of reagent required in each case and the final volume of the titrated solution 200 ml.

29. Hydrocyanic acid is ionized to 0.01 per cent in 0.1 *N* solution. Compute the ionization constant.

30. Formic acid has an ionization constant of 2.0×10^{-4}. Compute the percentage ionization of 0.1 *N* formic acid solution. Compute the *p*H value of 0.1 *N* formic acid and also that of a solution which is 0.1 *N* with respect to formic acid and 3.0 *N* with respect to sodium formate.

31. The ionization constant of ammonia, $\frac{[NH_4^+] \times [OH^-]}{[NH_3]}$, is 1.75×10^{-5}. Compute the *p*H value (*a*) of a solution containing 0.2 mole of dissolved NH_3 per liter and (*b*) the same solution after adding 4 moles of NH_4Cl.

32. How much sodium acetate must be added to a liter of water containing 6.5 milliequivalents of acetic acid to make the *p*H = 6?

33. A mixture of $BaCO_3$ and Li_2CO_3 reacts with the same volume of 0.1 *N* acid as if it were pure $CaCO_3$. Find the percentage Li_2O present. (*Hint.* Let x = the milliequivalents of one of the carbonates in a sample weighing 1 g. How many milliequivalents correspond to 1 g of $CaCO_3$?)

34. A substance reacts basic and may contain sodium carbonate, caustic soda, and sodium bicarbonate. Assuming that the last two substances cannot both be present, compute the percentage of each alkaline constituent from the following data: 1.160 g of the powder reacts with 26.27 ml of third-normal HCl when phenolphthalein is used in the cold, and with 59.17 ml if methyl orange is the indicator.

35. A mixture of Na_2HPO_4 and NaH_2PO_4 with an inactive impurity gives the following results: 1.2 g of powder reacts with 6.00 ml of 0.5 *N* HCl with methyl orange and with twice as much of 0.5 *N* base if phenolphthalein is used. Find the percentage composition of the original powder.

36. A sample of oleum dissolved in water gives H_2SO_4 equivalent to 108.5 per cent of the original weight. Find the percentage of free SO_3 and of total SO_3 in the oleum.

37. A substance contains sodium carbonate mixed with either sodium hydroxide or sodium bicarbonate together with some inert material. Compute the percentage of each of the above constituents present when: 1.500 g of sample reacts with 28.85 ml of 0.5 *N* HCl in the cold with phenolphthalein as indicator and with 23.85 ml more of the acid if methyl orange is the indicator.

38. A substance may contain the constituents listed in Problem 37 but nothing else of alkaline reaction. Compute the percentage of each of these substances. One gram of sample reacts with 17.96 ml of 1.038 *N* HCl with phenolphthalein as indicator and with 21.17 ml if methyl orange is used.

39. Another mixture, of character similar to that described in Problem 37, reacts with 20.0 ml of 0.6 *N* HCl with phenolphthalein in the cold and with 24.6 ml more if methyl orange is the indicator. The sample weighed 1.6 g. Compute the percentage composition.

40. Mixtures for student analysis are made from HCl, NaOH, and H_3PO_4 solutions. In each case the student is given 50-ml portions for analysis and asked to compute the weight of each of the following substances per liter, assuming that not more than two of these substances can be present in the same solution: HCl, H_3PO_4, NaOH, Na_2HPO_4, Na_3PO_4, NaH_2PO_4.

Sample 1. The solution reacts with 25 ml of 0.6 *N* NaOH when methyl orange is the indicator and with 48 ml of the NaOH solution when phenolphthalein is the indicator.

Sample 2. The solution reacts with 30 ml of 0.5 *N* HCl with phenolphthalein as the indicator and with 48 ml of the same acid when methyl orange is used.

Sample 3. The solution reacts with 25 ml of 0.6 *N* NaOH when methyl orange is used and with 75 ml of the same base when phenolphthalein is the indicator.

Sample 4. The solution reacts with 25 ml of 0.5 *N* acid with phenolphthalein, and 75 ml of acid are used with methyl orange.

Sample 5. The solution reacts with 25 ml of 0.6 *N* NaOH when phenolphthalein is present and with 30 ml of 0.5 *N* acid when methyl orange is the indicator.

41. A solution of HCl is standard against pure $KH(IO_3)_2$, molecular weight = 389.9 (cf. pp. 72, 73). The iodate is dissolved in an aqueous solution of KI and $Na_2S_2O_3$. Calculate the normality of the HCl if 32.56 ml was used in titrating 0.5455 g of the standard.

42. Nitrates can be reduced to NH_3 by Devarda's alloy (50 per cent Cu, 5 per cent Zn, and 45 per cent Al) in NaOH solution. A sample of $NaNO_3$ is analyzed in this way and the resulting NH_3 distilled into 150 ml of 4 per cent boric acid solution. The weight of the sample is 1.400 g; 36.0 ml of 0.45 *N* HCl used is for titrating the $(NH_4)_2B_4O_7$ formed. Calculate the percentage purity of the $NaNO_3$.

CHAPTER V

OXIDATION AND REDUCTION: (*a*) POTASSIUM DICHROMATE METHODS

Oxidation and reduction processes are those in which the substance analyzed is either oxidized or reduced by means of the solution with which the titration is made. When hydrogen is oxidized by oxygen it is changed from the neutral condition to that of a positive valence (or polarity) of 1 and oxygen is reduced from the neutral condition to a negative valence (or polarity) or 2. In this, and all other cases, the equivalent weight of the element used in an oxidation-reduction reaction is the atomic weight divided by the change in polarity. When an atom in any complex molecule is subjected to a change in polarity (oxidized or reduced) the equivalent weight of the compound is the gram-molecular weight divided by the *change in polarity* of the oxidized or reduced element. If more than 1 atom of the reactive element is present in the molecule, the molecular weight is divided by the total change in polarity, that is, by the change in polarity multiplied by the number of atoms undergoing such change (cf. p. 37).

Potassium dichromate is one of the well-known oxidizing agents used in volumetric analysis. It reacts, for example, with ferrous, stannous, or titanous salts and is reduced, thereby, to trivalent chromic salt. Equations for the reduction of the dichromate ion and oxidation of ferrous ion, etc., have been given on p. 38. Expressed in terms of electrons, e, the equation for the reduction of dichromate can be written

$$Cr_2O_7^{--} + 14H^+ + 6e = 2Cr^{+++} + 7H_2O$$

and that of the oxidation of ferrous ion

$$Fe^{++} - e = Fe^{+++}$$

These equations represent what actually takes place when the reduction of the dichromate is accomplished at the cathode and the oxidation of the iron is brought about at the anode of an electrolytic cell. There are 6.06×10^{23} actual atoms of iron in a gram atom, and if we multiply the actual charge of the electron by 6.06×10^{23} we obtain the value 96,500 coulombs which is called a *faraday*. When 6 faradays of electricity pass through an electrolytic cell containing an acid solution of dichromate at the cathode and a ferrous salt at the anode, 1 mole of dichromate can be reduced and 6 moles of ferrous iron can be oxidized. The above equations, therefore, show that the equivalent weight of dichromate is one-sixth of its molecular weight and that of ferrous ion is one atomic weight. The equation

$$Cr_2O_7^{--} + 6Fe^{++} + 14H^+ \rightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O$$

represents six equivalent weights of both dichromate and iron.

The two following tables show the change in polarity of some of the more common oxidizing and reducing agents. In these tables *M* signifies the weight of 1 mole.

COMMON OXIDIZING AGENTS

Reagent	Polarity Change	Gain in Electrons*	Equivalent Weight
Cl_2	0 to −1	$2e$	$M/2$
Br_2	0 to −1	$2e$	$M/2$
I_2	0 to −1	$2e$	$M/2$
$K_2Cr_2O_7$	Cr^{VI} to Cr^{III}	$6e$	$M/6$
$KMnO_4$	Mn^{VII} to Mn^{++}	$5e$	$M/5$
$KMnO_4$	Mn^{VII} to Mn^{IV}	$3e$	$M/3$
$KBrO_3$	Br^V to Br^-	$6e$	$M/6$
KIO_3	I^V to I^-	$6e$	$M/6$
$KClO_3$	Cl^V to Cl^-	$6e$	$M/6$
Cu	Cu^{++} to Cu^+	$1e$	M
Na_2O_2	O_2^{--} to $2O^{--}$	$2e$	$M/2$
concd. HNO_3	N^V to NO_2	$1e$	M
HNO_3	N^V to NO	$3e$	$M/2$
H_2O_2	O_2^{--} to $2O^{--}$	$2e$	$M/2$

COMMON REDUCING AGENTS

Reagent	Polarity Change	Loss in Electrons	Equivalent Weight
$FeSO_4$ (or any ferrous salt)	Fe^{++} to Fe^{+++}	$1e$	M
$SnCl_2$	Sn^{II} to Sn^{IV}	$2e$	$M/2$
HI	I^- to I°	$1e$	M
Zn	Zn° to Zn^{++}	$2e$	$M/2$
H_2O_2	O_2^{--} to O_2°	$2e$	$M/2$
H_2S	S^{-2} to S°	$2e$	$M/2$
$C_2O_4^{--}$	$C_2O_4^{--}$ to $2CO_2$	$2e$	$M/2$
$S_2O_3^{--}$	$2S_2O_3^{--}$ to $S_4O_6^{--}$	$2e$	M
$HAsO_3^{--}$	As^{III} to As^V	$2e$	$M/2$
SO_3^{--}	S^{IV} to S^{VI}	$2e$	$M/2$
As_2O_3	As^{III} to As^V	$4e$	$M/4$
$TiCl_3$	Ti^{III} to Ti^{IV}	$1e$	M
Fe	Fe° to Fe^{++}	$2e$	$M/2$
Fe dissolved in acid	Fe^{++} to Fe^{+++}	$1e$	M

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* The letter *e* is used in this book to designate a milliequivalent and also, as in this table, to designate an electron. In oxidation-reduction reactions the milliequivalents are determined by the loss or gain of electrons as the table shows.

From these tables of equivalent weights it is easy to write equations and compute results. It is not necessarily true that there will be a definite reaction between any given reducing agent and any oxidizing agent. Thus the oxidation of $S_2O_3^{--}$ to $S_4O_6^{--}$ will go easily with iodine solution but does not take place in the same way with permanganate although permanganate can be standardized indirectly against thiosulfate by allowing the permanganate to liberate I_2 from KI in acid solution and titrating the liberated I_2 with thiosulfate. Under certain conditions, $HAsO_3^{--}$ can be oxidized to $HAsO_4^{--}$ by MnO_4^- in acid solution. The tables show that $HAsO_3/2$ and $MnO_4/5$ are equivalents; therefore,

$$5HAsO_3^{--} + 2MnO_4^- + 6H^+ \rightarrow 5HAsO_4^{--} + 2Mn^{++} + 3H_2O$$

In such equations, when the oxidizer and reducer have been balanced and the proper products placed on the right-hand side, if there are then more positive charges on the right than on the left, add the requisite number of H^+ to the left side. If there are already more positive charges on the left, add water and form H^+ therefrom on the right. One must bear in mind, however, the conditions under which the reaction takes place and not form H^+ on the right if the solution is kept alkaline or use H^+ on the left if the solution is alkaline. In such cases OH^- can be formed on the right or added to the left side of the equation. Sometimes H_2O should be added to one side of the equation and H^+ or OH^- on the other.

ELECTROCHEMICAL THEORY OF OXIDATION-REDUCTION

Some of the reactions of acidimetry and alkalimetry are best understood by considering the ionization constants of the acids and bases and by applying the mass-action principle to the ionization of weak acids and bases. The strength of an acid, or of a base, can be expressed either in terms of these ionization constants or of the *p*H values of solutions of the same normal concentration. Thus if we were to take tenth-normal solutions of all acids and bases, measure the *p*H value of each of these solutions, and make a table arranging these acids and bases in order corresponding to increasing *p*H, we should find at the top of the table the strong mineral acids, HCl and HNO_3, with a *p*H of nearly 1 in tenth-normal solution, and at the bottom of the table the alkali hydroxides with a *p*H of nearly 13.

In such a table, we would find that the *p*H of a tenth-normal solution of an acid becomes larger as the ionization constant diminishes and the *p*H of a tenth-normal solution of a base becomes smaller as its ionization constant diminishes.

A salt of a weak acid added to a solution of a stronger acid raises the pH value; for example, we find that sodium acetate added to a solution of hydrochloric acid reduces the hydrogen-ion concentration and in that sense neutralizes the hydrochloric acid. When the difference in the ionization constants of two acids varies by about 10^4 it takes only a very small quantity of the stronger acid to furnish as many hydrogen ions as a fairly large quantity of the weaker acid does, and we can titrate all of the stronger acid before an appreciable quantity of the weaker acid reacts with the added base; if at some part of the solution some of the weaker acid is neutralized, the salt formed will at once enter into equilibrium with the hydrogen ions from the stronger acid, so that the final effect will be that only the strong acid is neutralized at the first end point.

In considering the reactions of oxidation-reduction it is useful to prepare a table to show the relative strengths of the various oxidizing and reducing agents. Just as all acids and bases can be classified in a common table on the basis of the pH values, so it is possible to prepare a single table which will show the tendency of each substance to undergo oxidation or reduction. Such a table can be called a *potential series.* It has been called a table of *oxidation potentials.* Just as we could use the concentration of OH^- as a basis of comparing dilute solutions of acids and bases instead of the concentration of H^+, because the product $[H^+] \times [OH^-]$ is equal to 10^{-14} in every solution at room temperature, so we can call the table one of *reduction potentials* since oxidation is just the opposite to reduction and all we have to do is to change the sign. In some textbooks, the same table is called one of *electrode potentials.* Whatever the table may be called, it is customary to place the strong reducing agents at the top of the list and end with the strong oxidizing agents. Thus, in considering the free elements with respect to their tendencies to undergo oxidation or reduction, we place the alkali metals at the top and the non-metal oxygen followed by fluorine at the bottom.

It has already been pointed out that a substance is said to be oxidized or reduced when some atom it contains has undergone a change in polarity. Oxidation results when the polarity is increased, and reduction when the polarity is decreased. In terms of the electron theory, an increase in polarity means the loss of one or more electrons by an atom. Our definition of oxidation, therefore, has lost its original significance of necessarily having something to do with oxygen. The atom of oxygen is believed to consist of a nucleus around which eight electrons are circulating, probably in elliptical orbits. The path of the first two electrons, like that of the electrons around the helium nucleus, lies closer to the nucleus than that of the other six electrons, and we say that oxygen belongs in Family VI of the periodic table. When oxygen enters into combination with another element to form an oxide other than a peroxide, it accepts two electrons from the other element. Even if there is no ionization of the oxide molecule, it is reasonable to assume that the oxygen is negative with respect to the other element and that it has become negative by receiving electrons. Thus, in the water molecule, we are accustomed to think of the hydrogen as being positive to the oxygen although the electron of each hydrogen atom may be merely shared with the oxygen. Whenever, therefore, any atom gives up one or more of its electrons to some other atom, or even if it merely shares one or more of its electrons with some other atom, the atom to which the electron or electrons originally belonged is said to be oxidized and the element offered the electron is said to be reduced.

This electronic conception of oxidation and reduction makes it easy to see why an oxidation is always accompanied by a reduction. A transfer of electrons takes place whenever an electric current flows through an aqueous solution containing an electrolyte. At the anode, where electrons pass from the solution to the wire, some substance is oxidized. This oxidation may be the liberation of oxygen gas, the liberation of halogen gas, the dissolving of a metal electrode, the deposition of a higher oxide such as PbO_2 or MnO_2 upon the anode, or the oxidation of some substance present in the electrolyzed solution such as a ferrous salt. At the same time that an oxidation takes place at the anode, electrons enter the solution at the cathode and a reduction takes place. This reduction may be the deposition of copper upon the cathode, the liberation of hydrogen gas, or the reduction of some substance in solution such as ferric salt, permanganate, or chromate. The only difference between oxidation and reduction of a titration and that of an electrolysis is that the reactions take place side by side in a titration and at some distance apart during electrolysis. Moreover, a chemical reaction of oxidation-reduction can be used as a source of an electric current, as will be explained.

If we place a piece of zinc in a solution of zinc sulfate and a piece of copper in a solution of copper sulfate and connect the two solutions by means of an inverted U-tube containing ammonium chloride solution, there will be no appreciable reaction until the copper and zinc are connected by a wire outside the solutions. Then a current will flow, electrons will pass from the wire to the solution and deposit copper, and electrons will leave the zinc and pass to the wire, forming zinc ions in the solution. The zinc, according to our definition, is oxidized and the copper is reduced; the two reactions take place simultaneously, and the effect is the same as if the piece of zinc were placed directly in the copper sulfate solution except that then we would not get any evidence of an electric current. In precisely the same way we can produce an electric current by making use of the reaction between potassium dichromate and some substance that it oxidizes, such as hydrogen sulfide or ferrous chloride. To get the electric current in a wire, we must place the acid solution of dichromate in one vessel and the hydrogen sulfide or ferrous salt in another. We must provide some indifferent electrolyte between the two solutions, and place an insoluble electrode in each solution. Then, as soon as the electrodes are connected by a wire, a current will flow. The dichromate will be reduced in one vessel and the hydrogen sulfide or ferrous salt will be oxidized in the other, and the final effect will be exactly the same as if the dichromate solution were added directly to the solution of the ferrous salt.

The potential series of the elements, therefore, can be expanded to include almost every reaction of oxidation or reduction, although, to be sure, it is sometimes difficult to measure the electrode potentials and many of them are not known with any degree of exactness. The measurement of the potentials, as will be explained more in detail in the chapter on *potentiometric titrations*, is usually accomplished by measuring the potential difference between two electrodes of which one is a standard half-cell of definitely known potential.

These potentials enable one to predict whether a given oxidation is likely to take place to completion so that it can be used in quantitative analysis. They do not tell, however, whether the speed of the reaction is sufficiently high to make the process satisfactory. Thus permanganate should be able to oxidize the reduced forms of substances listed about 0.15 volt higher in the table, but often the reaction takes place too slowly, as in the reaction with oxalic acid at room temperature. The presence of a catalyst is often needed.

The mass-action law applies to every oxidation-reduction reaction, and it is important that the beginner should understand this application. It will be shown in the chapter devoted to the *theory of electrolysis* that the potential of a metal against a solution of its ions is governed by the mathematical expression

$$E_{30} = E_0 + \frac{0.060}{n} \log c$$

when E_{30} is the observed electrode potential at 30°, E_0 is the potential given in the table (corresponding to the potential of the metal in a molal solution of its ions), n is the change in polarity, and c is the concentration of the ions expressed in moles per liter. The value 0.060 is a constant which varies with the absolute temperature; at 25° it is 0.059 and at 18° it is 0.058. The equation shows that the observed potential goes downward by 0.060 volt for a change of valence of one, or 0.030 volt for a valence change of two, when the concentration of the ions in the solution is 0.1 molal instead of molal. This means that the metal is easier to oxidize when the solution does not contain many of its ions and harder to deposit by electrolysis.

The student may notice that the above equation is sometimes written with a negative sign on the right-hand side. It is a purely arbitrary decision whether a given potential is called positive or negative with respect to hydrogen, and depends entirely on the definition of what is meant by *positive*. The chemist usually thinks of the elements at the top of the column as positive elements, but in making up an electrolytic cell, the positive-to-negative direction of the current *in the wire* is always from the lower to the higher member of the series. Thus, in the Daniell cell, the physicist considers the zinc immersed in zinc sulfate solution the negative element and the copper immersed in copper sulfate solution the positive element. Zinc is positive to copper in the solution, and copper is positive to zinc in the wire. When the signs are changed the *oxidation* potential becomes the *reduction* potential. With reduction potentials the above equation, p. 93, becomes

$$E_{30} = E_0 - \frac{0.060}{n} \log c \quad \text{or} \quad E_{30} = E_0 + \frac{0.060}{n} \log \frac{1}{c}$$

The following table gives the oxidation potentials of some of the common substances which easily undergo oxidation or reduction. Some of the potentials are not known exactly, but the relative position in the table is right in most cases. The values of E_0 apply when the concentrations of both the oxidized and reduced forms are equal to 1 molal. If the hydrogen ion enters into the reaction, the values correspond to the presence of sufficient hydrogen ions to make the solution molal. The concentration of water is assumed to be constant and not changed appreciably by the progress of the reaction. The letter e in the equilibrium expressions represents a " gram electron " or electricity corresponding to 1 faraday = 96,500 coulombs or 26.82 ampere-hours.

The electrode reaction for a simple case of oxidation-reduction in which no other substance participates can be written

$$\text{Ox} + n\,e \rightleftarrows \text{Red}$$

when Ox represents one mole of the oxidized form, Red one mole of the reduced form, n the change in polarity, and e the electron (faraday in case of the gram atom). The equilibrium between a metal and its ions is a special case in which the metal represents the reduced form, and since the metal as such is insoluble in water, its concentration does not enter into consideration. The equilibrium is the same whether we take a wire or a thick rod of the metal. If, however, the substance exists to an appreciable extent dissolved in the solution, the concentration of both Ox and Red has an effect upon the final state of equilib-

NORMAL OXIDATION POTENTIALS

Oxidized Form	Reduced Form	Change in Polarity	Electrode Reaction	Normal Potential or E_0 in Volts
K^+	K	1	$K^+ + e \rightleftarrows K$	−2.92
Ca^{++}	Ca	2	$Ca^{++} + 2e \rightleftarrows Ca$	−2.7
Mg^{++}	Mg	2	$Mg^{++} + 2e \rightleftarrows Mg$	−2.40
Zn^{++}	Zn	2	$Zn^{++} + 2e \rightleftarrows Zn$	−0.76
Fe^{++}	Fe	2	$Fe^{++} + 2e \rightleftarrows Fe$	−0.43
H^+	$\frac{1}{2}H_2$	1	$H^+ + e \rightleftarrows \frac{1}{2}H_2$	−0.00
SO_4^{--}	S^{--}	8	$SO_4^{--} + 8H^+ + 6e \rightleftarrows S + 4H_2O$	?
Ti^{++++}	Ti^{+++}	1	$TiO^{++} + e \rightleftarrows Ti^{+++}$	+0.04
SO_4^{--}	H_2SO_3	2	$SO_4^{--} + 4H^+ + 2e \rightarrow H_2SO_3 + H_2O$	+0.14
$\frac{1}{2}S_4O_6^{--}$	$S_2O_3^{--}$	1	$\frac{1}{2}S_4O_6^{--} + e \rightleftarrows S_2O_3^{--}$	+0.13
Sn^{++++}	Sn^{++}	2	$Sn^{++++} + 2e \rightarrow Sn^{++}$	+0.14
S°	H_2S	2	$S^\circ + 2H^+ + 2e \rightarrow H_2S$	+0.17
Cu^{++}	Cu	2	$Cu^{++} + 2e \rightleftarrows Cu$	+0.34
UO_2^{++}	U^{++++}	2	$UO_2^{++} + 4H^+ + 2e \rightleftarrows U^{++++} + 2H_2O$	+0.36
Cu^{++}	$CuCl_2^-$	1	$Cu^{++} + 2Cl^- + e \rightleftarrows CuCl_2^-$	+0.46
$Fe(CN)_6^{---}$	$Fe(CN)_6^{----}$	1	$Fe(CN)_6^{---} + e \rightleftarrows Fe(CN)_6^{----}$	+0.49
CO_2	$C_2O_4^{--}$	2	$2CO_2 + 2e \leftarrow C_2O_4^{--}$	?
$\frac{1}{2}I_2$	I^-	1	$\frac{1}{2}I_2 + e \rightleftarrows I^-$	+0.54
H_3SbO_4	H_3SbO_3	2	$H_3SbO_4 + 5H^+ + 2e \rightarrow Sb^{+++} + 4H_2O$ $H_3SbO_4 + H_2O + 2e \leftarrow H_3SbO_3 + 2OH^-$	?
H_3AsO_4	H_3AsO_3	2	$H_3AsO_4 + 2H^+ + 2e \rightleftarrows H_3AsO_3 + H_2O$	+0.57
HNO_2	NO	1	$NO_2^- + 2H^+ + e \rightleftarrows NO + H_2O$	+0.7?
Fe^{+++}	Fe^{++}	1	$Fe^{+++} + e \rightleftarrows Fe^{++}$	+0.75
HVO_3	VO^{++}	1	$VO_3^- + 4H^+ + e \rightleftarrows VO^{++} + 2H_2O$	+0.92
Dil. HNO_3	HNO_2	2	$NO_3^- + 2H^+ + 2e \rightleftarrows NO_2^- + H_2O$	+0.9
Conc. HNO_3	NO_2	1	$NO_3^- + 2H^+ + e \rightleftarrows NO_2 + H_2O$	?
IO_3^-	I^-	6	$IO_3^- + 6H^+ + 6e \rightleftarrows I^- + 3H_2O$	+1.09
$\frac{1}{2}Br_2$	Br	1	$\frac{1}{2}Br_2 + e \rightleftarrows Br^-$	+1.07
O_2	H_2O_2	2	$O_2 + 2H^+ + 2e \rightleftarrows H_2O_2$	+1.08
$Cr_2O_7^{--}$	$2Cr^{+++}$	6	$Cr_2O_7^{--} + 14H^+ + 6e \rightleftarrows 2Cr^{+++} + 7H_2O$	+1.195
$\frac{1}{2}O_2$	H_2O	2	$\frac{1}{2}O_2 + 2H^+ + 2e \rightleftarrows H_2O$	+1.23
MnO_2	Mn^{++}	2	$MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{++} + 2H_2O$	+1.33
$\frac{1}{2}Cl_2$	Cl^-	1	$\frac{1}{2}Cl_2 + e \rightleftarrows Cl^-$	+1.36
Ce^{++++}	Ce^{+++}	1	$Ce^{++++} + e \rightleftarrows Ce^{+++}$	+1.45
BrO_3^-	Br^-	6	$BrO_3^- + 6H^+ + 6e \rightleftarrows Br^- + 3H_2O$	+1.48
MnO_4^-	Mn^{++}	5	$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{++} + 4H_2O$	+1.52
MnO_4^-	MnO_2	3	$MnO_4^- + 4H^+ + 3e \rightleftarrows MnO_2 + 2H_2O$	+1.58
$S_2O_8^{--}$	$2SO_4^{--}$	2	$S_2O_8^{--} + 2e \rightleftarrows 2SO_4$	?
H_2O_2	H_2O	2	$H_2O_2 + 2H^+ + 2e \rightleftarrows 2H_2O$	+1.9
$NaBiO_3$	Bi^{+++}	2	$NaBiO_3 + 6H^+ + 2e \rightarrow Na^+ + Bi^{+++} + 3H_2O$	?
$\frac{1}{2}F_2$	F^-	1	$\frac{1}{2}F_2 + e \rightleftarrows F^-$	+2.8

rium. With these concentrations in moles per liter expressed as [Ox] and [Red], the expression for the normal potential becomes

$$E_{30} = E_0 + \frac{0.060}{n} \log \frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

The value E_0 is that given in the table where it is assumed that each concentration is that of a molal solution. Then since [Ox] = [Red] and the log of 1 = 0, the second term disappears and $E_{30} = E_0$.

If hydrogen or hydroxide ions take part in the reaction they also influence the final state of equilibrium. Thus, in the reaction $H_3AsO_4 + 2H^+ + 2e \rightleftarrows H_3AsO_3 + H_2O$, the potential is determined by the equation:

$$E_{30} = E_0 + \frac{0.060}{2} \log \frac{[H_3AsO_4]\,[H^+]^2}{[H_3AsO_3]}$$

and in the reaction $MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{++} + 4H_2O$ the potential is determined by the equation

$$E_{30} = E_0 + \frac{0.060}{5} \log \frac{[MnO_4^-]\,[H^+]^8}{[Mn^{++}]}$$

In these last two equations it is not necessary to take the H_2O into consideration because when the reaction takes place in a dilute solution the concentration of the water does not change appreciably as a result of the progress of the oxidation and reduction. The concentration of the hydrogen ions determines the final state of equilibrium to a marked degree in the above reactions. Thus, in a strongly acid solution, arsenic acid can be reduced quantitatively to arsenious acid by means of potassium iodide, but in a slightly alkaline solution, arsenite can be oxidized completely to arsenate by iodine. The above arsenate-arsenite equation can be written

$$E_{30} = E_0 + \left[\frac{0.060}{2} \log \frac{[H_3AsO_4]}{[H_3AsO_3]} + \frac{0.060}{2} \log\,[H]^2\right]$$

and in this form can be used to calculate the effect of changes in hydrogen-ion concentration or to calculate the effect of changes in the $[H_3AsO_4]$ to $[H_3AsO_3]$ ratio at a definite concentration of hydrogen ions.

With permanganate, the reduction products are different at different concentrations of hydrogen ions. Thus in acid solutions, Mn^{++} is the usual product; in neutral or slightly alkaline solutions MnO_2 is usually formed; and in strongly alkaline solutions green MnO_4^{--} is sometimes obtained. At 18°, the constant 0.060 becomes 0.058.

The use of the table of normal potentials can be illustrated by a few examples.

1. *If 100 ml of a solution contains only 0.06 mg of Cu ions, what will be the electrode potential of copper against this solution?* This question is of importance in considering precipitation of copper by a baser metal such as iron or in considering the electrolytic deposition of copper. As the solution becomes dilute, it becomes harder to precipitate copper, but since we usually weigh only to 0.1 mg we can call the precipitation of the copper complete when only 0.06 mg remains in 100 ml of solution. Such a solution is 10^{-5} molal in Cu^{++}. We find in the table that E_0 for Cu is +0.34 volt. Then E, the desired potential, can be computed from the equation

$$E_{30} = +0.34 + \frac{0.060}{2} \log 10^{-5} = +0.34 - 0.15 = +0.19 \text{ volt}$$

Since this value is below that of hydrogen, it follows that copper can be deposited completely from a solution containing acid either by metallic iron or by electrolysis. If the value had come out greater than 0.00, it would have been proved impossible to precipitate all the metal in the presence of a normal solution of hydrogen ions.

2. *What will be the oxidation potential of Fe^{+++}/Fe^{++} in a solution containing 0.28 g of iron in 250 ml of solution when all but 0.028 mg is present in the ferric condition?* In titration analyses we try to work to an accuracy of 1 part in 1,000. If, therefore, we attempt to analyze a solution by measuring the volume of oxidizing reagent required to oxidize the iron from the ferrous to the ferric state we can call the reaction complete when only 1 part in 10,000 of unoxidized ferrous salt remains. As the ferrous ions are oxidized the reduction potential of Fe^{+++}/Fe^{++} falls, and it is desirable to know whether it will fall to such a low value that a given oxidizing agent will no longer exert an oxidizing effect. In this case, $[Fe^{+++}] = 2 \times 10^{-2}$; $[Fe^{++}] = 2 \times 10^{-6}$ mole per liter.

$$E_{30} = +0.75 + 0.060 \log \frac{2 \times 10^{-2}}{2 \times 10^{-6}} = +0.75 + 0.24 = +0.99 \text{ volt}$$

3. *If 200 ml of tenth-normal ferric ions is treated with 200 ml of tenth-normal stannous ions, will the reduction of the ferric ions and oxidation of the stannous ions be practically complete?*

In the reduction of a solution of ferric chloride with stannous chloride the reaction is complicated by the fact that ferric chloride and stannic chloride both form complexes with hydrogen chloride. To illustrate the use of the table of oxidation potentials, however, we shall assume that the reaction can be expressed as follows: $2Fe^{+++} + Sn^{++} \rightarrow 2Fe^{++} + Sn^{++++}$, and disregard the fact that ions such as $FeCl_4^-$ and $SnCl_6^{--}$ are present.

(1) The solution at the start is 0.1 molar in ferric ion and the solution is 0.05 molar in iron after stannous chloride is added. If after the addition of the stannous chloride the solution is only 5×10^{-5} molar in ferric ion we can call the reduction sufficiently complete for the purpose of quantitative analysis because that corresponds only to an error of 1 part in 1000, which is as accurate as most titrations in volumetric analysis, and the concentration of $[Fe^{++}]$ will be $5 \times 10^{-2} - 5 \times 10^{-5}$, or, since the calculation is not good to more than three significant figures, we can say $[Fe^{++}] = 5 \times 10^{-2}$. Then, since the equivalent weight of tin in this reaction is one-half the atomic weight, the corresponding concentrations in moles per liter are: $[Sn^{++}] = 2.5 \times 10^{-5}$; $[Sn^{++++}] = 2.5 \times 10^{-2}$.

In the table of normal potentials on p. 95 we find the values $Fe^{+++}/Fe^{++} = +0.75$ volt and $Sn^{++++}/Sn^{++} = +0.14$. Then, applying the Nernst theorem we have, at 18°:

$$E_{Fe} = +0.75 + 0.060 \log \frac{5 \times 10^{-5}}{5 \times 10^{-2}} = +0.75 - 0.18 = +0.57 \text{ volt}$$

$$E_{Sn} = +0.14 + \frac{0.060}{2} \log \frac{2.5 \times 10^{-2}}{2.5 \times 10^{-5}} = +0.14 + 0.090 = +0.23 \text{ volt}$$

This computation shows that the oxidation potential of the Fe^{+++}/Fe^{++} is still below that of Sn^{++++}/Sn^{++} and the ferric ions are still capable of oxidizing stannous ions even after 99.9 per cent of the original ferric ions have been reduced.

(2) The table can be used to compute what the concentrations of ferric and stannous ions will be when a state of equilibrium is reached on mixing, for example, 200 ml of tenth-normal ferric solution with 200 ml of tenth-normal stannous solution.

Let E' represent the Fe^{+++}/Fe^{++} potential and E'' the Sn^{++++}/Sn^{++} potential. When equilibrium is reached, $E' = E''$.

Let $x = [Fe^{+++}]$ and $x/2 = [Sn^{++}]$ at the state of equilibrium. Then $[Fe^{++}] = 0.05 - x$ and $[Sn^{++++}] = 0.025 - x/2$, but in these last two concentrations there will be no appreciable error if we call $[Fe^{++}] = 0.05$ and $[Sn^{++++}] = 0.025$. At equilibrium

$$E' = +0.75 + 0.060 \log \frac{x}{0.05} = E'' = +0.14 + 0.030 \log \frac{0.025}{x/2}$$

$$+0.75 + 0.060 \log x + 0.060 \log 20 = +0.14 + 0.030 \log 0.05 - 0.030 \log x$$

$$0.060 \log x + 0.030 \log x = 0.14 + (0.030 \times -1.30) - 0.75 - 0.060 \times 1.30$$

$$0.090 \log x = 0.14 - 0.039 - 0.75 - 0.078 = -0.72$$

$$\log x = -8.0$$

$$x = 1 \times 10^{-8} \text{ mole per liter}$$

In 400 ml, there will be $0.4 \times 56 \times 10^{-8} = 2.2 \times 10^{-7}$ g Fe^{++}.

This means that, when 200 ml of 0.1 N Fe^{+++} solution (1.12 g Fe^{+++}) is treated with 200 ml of 0.1 N Sn^{++} solution, the 400 ml of mixture will contain only an unmeasurable quantity of unreduced Fe^{+++}.

LABORATORY EXERCISES

Preparation and Standardization of Dichromate Solution

Prepare an approximately tenth-normal solution of potassium dichromate by dissolving not more than 5 g of the salt in water and diluting the solution to the volume of about 1 l.[1]

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[1] The dichromate solution can be made exactly tenth-normal by dissolving 4.903 g of pure $K_2Cr_2O_7$ in water, making up to exactly 1 l in a volumetric flask, and mixing well by pouring the solution back and forth from the flask to a dry beaker and back to the flask at least four times.

Prepare an approximately tenth-normal solution of ferrous ammonium sulfate by mixing 40 g of the crystals with 50 ml of 6 *N* sulfuric acid and diluting to about 1 l. The ferrous ions in this solution oxidize slowly from atmospheric oxygen that dissolves in the solution. The acid is necessary, therefore, to keep the salt in solution since the original salt contains acid combined with bivalent ferrous ions and not enough for the trivalent iron formed by oxidation. The strength of this solution will diminish slowly from day to day. The dichromate solution, on the other hand, is very stable.

To determine the relative strengths of the two solutions, fill a glass-stoppered buret with the dichromate solution, observing the usual precautions with respect to cleaning and rinsing, and fill a plain buret with the ferrous solution. Or, since the relative strengths of the two solutions change slightly from day to day and the determination may have to be repeated frequently, it is somewhat more convenient to use a 25-ml pipet for the ferrous solution, cleaning the pipet carefully (see p. 31) and rinsing it with three portions of the solution.

Run out from the buret about 40 ml of the ferrous solution into a beaker or flask of about 300-ml capacity. Add 10 ml of 6 *N* hydrochloric acid and 100 ml of water. Mix and titrate with the potassium dichromate solution.

Determination of the End Point. The end point of this titration can be determined in three ways: (1) by means of an external indicator, (2) by an internal indicator, and (3) by the potentiometer.

(1) The end point of the titration of ferrous ions with dichromate can be determined by taking a drop of the solution and testing it on a white porcelain " spot plate " with a drop of potassium ferricyanide solution. This method is capable of giving excellent results after a little practice. Objection can be raised that some of the solution is lost by taking out the drops of solution for the tests, and if the testing is started too soon, the loss may be appreciable. Since a drop of 0.05 ml is only 1/4000 of a total volume of 200 ml, this error is not serious if the iron content is less than 0.1 g when the first test is made. Another difficulty lies in the fact that a negative test for Fe^{++} in a single drop of solution does not prove positively that the entire solution contains less than 0.2 mg of Fe^{++} unless the test serves to indicate 0.00005 mg of Fe^{++} in the drop taken.

(2) Just as there are dyestuffs which change color at a definite *p*H value of an aqueous solution and serve as indicators in alkalimetry and acidimetry, so there are certain organic substances which change color as a result of oxidation or reduction. Diphenylamine, $(C_6H_5)_2NH$, diphenylbenzidine $[C_6H_4{\cdot}NH{\cdot}C_6H_5]_2$, and diphenylamine sulfonic acid, $(C_6H_5)NH(C_6H_4{\cdot}SO_3H)$, are such substances. Each of these is oxidized less readily than ferrous ions. During the oxidation of Fe^{++} by $Cr_2O_7^{--}$, the Fe^{++}/Fe^{+++} potential falls as the concentration of Fe^{++} becomes smaller and that of the Fe^{+++} becomes larger, or, in other words, it becomes harder for the oxidation to take place. There is not quite enough difference between the oxidation-reduction potentials of the Fe^{++}/Fe^{+++} and that of the above-mentioned organic

substances to insure that the oxidation of the Fe^{++} is complete before that of the amine starts, but this difficulty as well as the effect of yellow ferric chloride in the solution can be overcome by adding some phosphoric acid which removes Fe^{+++} and $FeCl_3$ from the solution, forming a colorless acid phosphate complex. On the other hand, it requires a measurable quantity of the dichromate solution to accomplish the oxidation of the organic compound. This causes a slight error in the opposite direction.

(3) Since the oxidation-reduction potential shown by a platinum electrode measured against a standard calomel cell changes sharply as soon as 1 drop of 0.1 *N* dichromate solution in excess is added, the potentiometer is capable of indicating a sharp end point in the titration of a ferrous solution with dichromate. This will be discussed at greater length in a later chapter of this book.

The student may choose either of the following two methods for determining the end point. It is important to use the same method in standardizing the solution as in the analysis because a slight excess of reagent causes a low standardization value and a high value in an analysis. A titration error, therefore, is compensated when the same error is made in the standardization and in the analysis. The compensation is exact when the same volume of reagent is used in the analysis as in the standardization.

1. Prepare a fresh solution of about 10 mg of pure potassium ferricyanide in 10 ml of distilled water. Do not attempt to use a solution that was prepared on another day. With a stirring rod, transfer small drops of this indicator solution to the cavities in a spot plate or to a paraffin coating on a white surface. When about 30 ml of the dichromate solution has been added from a buret, take out a drop of the solution on the end of a stirring rod and add it to a drop of the potassium ferricyanide solution. Wash the stirring rod before returning it to the solution. If the test shows a strong blue color, continue adding the dichromate in 1.0- to 0.25-ml portions until only a light blue test is obtained, and then test after each drop or two.

If the indicator solution has stood for some time and a little ferrocyanide is present, a good end point will not be obtained. If the indicator solution is too strong or more than a small drop is used, the test will appear green instead of blue owing to the yellow color of the reagent; and with a strong indicator solution a reddish appearance is sometimes obtained. It is best to add a series of small drops of indicator solution to the test plate and add the drops of titrated solution in regular sequence, noting the buret reading corresponding to each test made near the end point. Take as end point the first test in which a blue does not develop within 1 minute.

Compute the value of 1 ml of ferrous solution in terms of the dichromate solution by dividing the volume of dichromate solution required by the volume of ferrous solution taken.

2. To a carefully measured volume (30–40 ml) of the ferrous solution add 5 ml of phosphoric acid, *d* 1.7, and 0.3 ml of 0.01 *M* solu-

tion of the sodium salt of diphenylamine sulfonic acid, and dilute to about 300 ml.

To prepare the indicator solution, dissolve 0.32 g of the barium salt of diphenylamine sulfonic acid in 100 ml of water, add 0.5 g of sodium sulfate, mix, and allow the barium sulfate precipitate to settle. Decant off the clear solution. If this indicator is not available, a solution of 0.2 g diphenylamine in 100 ml of pure, concentrated sulfuric acid can be used instead.

Add the dichromate solution slowly while stirring until the original pure green color changes to a gray, a greenish gray, or a bluish green if considerable iron is present. From this point, add the dichromate 1 drop at a time until the first tinge of purple appears and remains on stirring. From the total volume of dichromate used, subtract 0.05 ml as a blank on the indicator. Divide the volume of dichromate required by the volume of ferrous solution taken to get the value of 1 ml of the latter in terms of the former.

The color change at the end point is easy to see with a little practice provided that the solution contains sufficient mineral acid and the phosphoric acid. When, however, an excess of dichromate is added, the mixture of yellow CrO_4^{--} (formed from $Cr_2O_7^{--}$ by hydrolysis), green Cr^{+++}, and the indicator does not assume a deeper purplish tint. Moreover, the gray, greenish gray, and bluish green shades mentioned above are not always noticed. With practice it is easy to tell whether the solution has the green color characteristic of the indicator and Fe^{++} or not. If it has not, and further addition of a little more $K_2Cr_2O_7$ produces no noticeable change, the only thing to do is to titrate back with standard Fe^{++} solution until a clear light green color is obtained and then finish by adding more $K_2Cr_2O_7^{--}$ until the purple tint is seen.

Standardization of the Dichromate Solution. Potassium dichromate can be obtained sufficiently pure to serve as a standard. A solution of potassium dichromate of known strength, therefore, can be obtained by weighing out the requisite quantity of the pure, recrystallized salt (4.904 g for 1 l of tenth-normal solution) into a volumetric flask, dissolving in a little water, diluting up to the mark, and mixing thoroughly by pouring back and forth at least four times into a beaker which is clean and dry at the start. The solution can be standardized in three ways: (1) against a sample of pure ferrous ammonium sulfate, (2) against a sample of pure iron wire or iron of known purity, or (3) against a ferrous solution which has been titrated within a few hours against a solution of potassium permanganate which has been standardized recently against sodium oxalate. If the first method is chosen, it is always well to test the solution after it has been prepared by one of the other methods.

Against the second method of standardization, objection has been raised that it has been found difficult to prepare absolutely pure iron. Moreover, the impurity present may be oxidizable so that if the purity of the sample is known it is also desirable to know what the impurities are. Electrolytic iron, therefore, has been recommended, but even this is sometimes impure and it is troublesome to ask each student to prepare his own material. If the sample of iron is in contact with moist air, it rusts quickly. Similarly with respect to the ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, or ferrous sulfate, $FeSO_4 \cdot 7H_2O$, it is possible to purchase samples which are at least 99.9 per cent pure; but if the open bottle is allowed to stand in the air, some water of crystallization is usually lost and salts with water of crystallization are not ideal standards. For the purposes of instruction, "iron for standardization" or pure ferrous ammonium sulfate (Mohr's salt) can be used satisfactorily, but the student should bear in mind that, although the results of his analyses may agree perfectly, the actual values may be as much as 0.25 per cent of the total iron content in error when these faulty standards are used.

1. **Standardization against Pure Ferrous Ammonium Sulfate.** Weigh out portions of 1.5–2.0 g of pure Mohr's salt, recording the weight to the nearest milligram. Add 10 ml of 6 *N* hydrochloric acid, dilute and titrate promptly with potassium dichromate solution, using the same method of determining the end point as that chosen for the preliminary titration of dichromate against ferrous sulfate solution (p. 100). If the solution stands long it will become oxidized to some extent and become useless as a standard.

Since the equivalent weight of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ is the molecular weight, 392.13, the normal concentration N of the dichromate solution will be found by the formula $p/(n \times 0.3921) = N$ when n ml of dichromate is used in titrating p g of pure ferrous ammonium sulfate.

2. **Standardization against Iron.** Weigh out accurately 0.24- to 0.26-g portions of pure, bright iron wire, handling it as little as possible, rolling it up so that it will not interfere with the free movement of the balance and discarding any rusty wire. Drop each weighed portion of wire into an Erlenmeyer flask containing 30 ml of 6 *N* hydrochloric acid. Place a small watch glass on the flask or, still better, a stemless, 40-mm funnel in the neck, and heat gently until all the wire is dissolved. Wash down the sides of the flask with a little hot water, and add stannous chloride from a dropper until the solution is colorless,[1] but avoid adding an

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[1] There is usually a slight oxidation of the iron and formation of yellow ferric chloride, unless special pains are taken to exclude air during the heating and cooling.

$$4Fe^{++} + O_2 + 4H^+ \rightarrow 4Fe^{+++} + 2H_2O \qquad Fe^{+++} + 3Cl^- \rightleftarrows FeCl_3$$

The stannous chloride reduces the ferric salt:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

and the excess reducing agent reacts with mercuric chloride to form a precipitate of mercurous chloride: $SnCl_2 + 2HgCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$, provided that a conexcess. Dilute with 150 ml of water, cool under the water faucet, and add 10 ml of mercuric chloride solution. Allow to stand about 2 minutes and titrate with dichromate, determining the end point as described on p. 100.

From the net volume of potassium dichromate solution, n ml, required to oxidize a solution of ferrous salt from p g of iron wire, compute the normality of the dichromate solution as follows:

$$\frac{p}{n \times 0.05584} = N$$

3. **Indirect Standardization against Sodium Oxalate.** Either of the above methods of standardization will give results which are sufficiently accurate for practice with the potassium dichromate titrations. If, however, it is desired to get results which will be correct within less than 0.25 per cent of the total iron content (*e.g.*, if it is desired in the analysis of an iron ore containing 60 per cent Fe_2O_3 to get results which are within less than 0.15 per cent of this value), neither method is satisfactory. If the bottle containing the ferrous ammonium sulfate is left standing exposed to the air, and this will happen when a sample is kept in a phial under a cork stopper because cork, unless paraffined, is not impervious to air, there will be a gradual efflorescence of the crystals and as a result the iron content will become greater than the theoretical value of the pure salt. When iron wire is used as a standard, there may be some unobserved rust on the wire or there may be sufficient impurity in the metal to affect the results appreciably.

The Bureau of Standards will furnish at a reasonable price a sample of sodium oxalate which, when handled as directed, may be regarded as better than 99.99 per cent pure. The reaction between sodium oxalate and potassium dichromate cannot be used to serve as a *direct* method of standardization. In cold, dilute acid solutions, the oxalate ion is not oxidized quantitatively by dichromate. An indirect method, however, can be used.

Procedure. Standardize a solution of potassium permanganate against pure sodium oxalate as directed on p. 111. With the aid of a pipet, transfer 25-ml portions of a ferrous sulfate solution (see p. 99) to each of four 400-ml beakers or 300-ml Erlenmeyer flasks. Titrate two of these portions against the potassium permanganate solution which has just been standardized and the other two portions against the potassium dichromate solution. Then if a ml of N_a-normal perman-

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siderable excess of mercuric chloride is added. If, however, too much stannous chloride is present, some metallic mercury is precipitated;

$$SnCl_2 + HgCl_2 \rightarrow SnCl_4 + Hg$$

and the analysis is spoiled, because the precipitated mercury dissolves in acid when an oxidizing substance is present. The mercurous chloride precipitate should be white and silky in appearance; if it is dark colored, discard the solution.

As reagents use a solution of 50 g $SnCl_2 \cdot 2H_2O$ in 100 ml of concentrated hydrochloric acid, and a solution of 27 g mercuric chloride in a liter of water.

ganate are used and b ml of the dichromate solution, the normal concentration, N_b, of the latter is $(a/b) \cdot N_a = N_b$. Each of the above titrations should agree within 2 parts in 1000 of its duplicate, and the final results should be within 0.2 per cent of the truth.

Determination of Iron in Limonite

Weigh out accurately to four decimal places about 0.5 g of finely powdered ore into a small porcelain crucible. Using a small flame, roast the ore at dull redness for 5 minutes to destroy organic matter. Allow the crucible to cool, transfer the limonite to a small beaker, and remove the stain in the crucible by heating with four 5-ml portions of 6 N hydrochloric acid. Heat the limonite with the acid until the residue no longer shows the limonite color. Add stannous chloride dropwise to the hot solution until the yellow color due to ferric chloride disappears and the solution is nearly colorless,[1] but avoid an excess. If more than 1 drop in excess is added, add a little potassium permanganate till a yellow color is obtained and repeat the reduction. Cool, dilute to 50 ml, and quickly add 8 ml of saturated mercuric chloride solution. Wait 3 minutes to make sure that the reaction is complete, transfer to a larger beaker, dilute to about 300 ml, and titrate with dichromate without further delay.

Determination of Chromium in Chromite

By fusion with sodium peroxide, the trivalent chromium is oxidized to chromate:

$$2FeCr_2O_4 + 7Na_2O_2 \rightarrow 2NaFeO_2 + 4Na_2CrO_4 + 2Na_2O$$

When the melt is leached with water, the iron is precipitated as ferric hydroxide and the chromate dissolves:

$$NaFeO_2 + 2H_2O \rightarrow NaOH + Fe(OH)_3$$

It is well to add a little more peroxide to make sure that the chromium is fully oxidized. Then the excess peroxide is decomposed by boiling the alkaline solution, the precipitate is dissolved in sulfuric acid, a known volume of standard ferrous sulfate is added, and the excess ferrous salt is titrated with dichromate.

Weigh out 0.3–0.5 g of ore into a 30–35 ml iron crucible and mix with about 4 g of sodium peroxide, using a dry stirring rod. Remove any adhering powder from the rod by stirring about 1 g of sodium peroxide with it. Cover the mixture in the crucible with this last portion of peroxide. Place the lid on the crucible, gradually heat the contents to the melting point, and maintain the fusion temperature for 5–6 minutes. Allow the melt to cool, place the crucible in a 300-ml beaker, and add 150 ml of cold water, keeping the beaker covered to avoid loss by effervescence.

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[1] The addition of 3 ml of 0.5 per cent stannous chloride solution will hasten the dissolving of the limonite. It is important to avoid an excess of stannous chloride which will cause reduction of mercuric chloride to mercury and spoil the analysis. The roasting in the porcelain is unnecessary if the ore contains no organic matter. Sometimes a little Na_2CO_3 added to the ore before the roasting helps to make the sample dissolve more readily in acid.

When the fused mass has disintegrated, remove the crucible and wash it thoroughly. Add 0.5 g more of peroxide and gradually heat the liquid to boiling. Boil very gently for 15 minutes to make sure that all peroxide is decomposed. Allow the solution to cool somewhat, make distinctly acid to litmus, and add 10 ml of 6 N sulfuric acid in excess. Dilute to 200 ml and add, from a clean pipet, which has been rinsed three times with a little of the solution, 25 ml of standard (approximately 0.1 N) ferrous ammonium sulfate solution. Stir and test a drop of the solution on a white surface with fresh potassium ferricyanide solution. If no blue color is obtained, add another 25-ml portion of ferrous salt and continue adding it until an excess is present. Then titrate the excess with 0.1 N potassium dichromate solution.

On the same day that the analysis is made, take 25 ml of the ferrous solution, dilute to 300 ml, add 10 ml of 6 N sulfuric acid, and titrate with potassium dichromate solution. Compute the percentage of chromium present as follows:

Let a = milliliters of N-normal $K_2Cr_2O_7$ required to neutralize one pipetful of ferrous solution.
b = number of pipetfuls of ferrous solution used.
n = milliliters of $K_2Cr_2O_7$ used in the final titration.
s = weight of sample.
e = milliequivalent weight (0.01734 g Cr; 0.02534 g Cr_2O_3; 0.03731 g $FeCr_2O_4$).

$$\frac{(a \cdot b - n)N \times e \times 100}{s} = \%$$

The analysis can be made with diphenylamine sulfonic acid as indicator. In this case it is necessary to add phosphoric acid, and proceed as described on pp. 100, 101 after adding enough ferrous salt to give a clear blue color to the solution.

HOME PROBLEMS

43. What weights of iron ore should be taken for analysis (a) that the percentage of Fe is the same as the milliliters of 0.09 N $K_2Cr_2O_7$ used and (b) that the percentage of Fe_2O_3 is the same as the milliliters of dichromate used?

44. In the analysis of an aluminosilicate containing only ferrous Fe, 0.48 g of Fe_2O_3 and Al_2O_3 was obtained from 1.4 g of silicate. The mixed oxides, analyzed like limonite, contained iron enough to react with 25 ml of $K_2Cr_2O_7$ solution of which 1 ml = 0.0373 g of pure Mohr's salt. Find the percentage of FeO and of Al_2O_3 in the silicate.

45. One hundred milliliters of $K_2Cr_2O_7$ solution (10 g per liter), 5 ml of 6 *N* H_2SO_4, and 75.0 ml of $FeSO_4$ solution, containing 80 g of $FeSO_4 \cdot 7H_2O$ per liter, are mixed and titrated with 0.2121 *N* $K_2Cr_2O_7$. How many milliliters are required?

46. In the analysis of a sample of chromite the sample weighed 0.45 g; after fusion with peroxide it was treated with 35 ml of 0.5 *N* ferrous solution, and the excess of this solution reacted with 30 ml of 0.12 *N* dichromate solution. Find the percentage of Cr and Cr_2O_3.

47. Using the same two standard solutions and the same volume of ferrous solution as in Problem 46, what weight of chromite should be taken such that the percentage of Cr can be determined by subtracting the volume of dichromate used from a certain number? What is the "certain number?" (See formula above.)

48. Answer the same question to get the percentage of Cr_2O_3 by a similar subtraction.

49. If 50.00 ml of 0.09 *N* dichromate solution is reduced by a certain reducing agent and the reduced solution treated with 50.00 ml of 0.08 *N* ferrous sulfate solution to reduce the Cr completely to the trivalent condition, find the valence of the Cr in the original reduced state if 27.8 ml of the original dichromate solution is required to oxidize the excess of ferrous solution after the last reaction.

Hint. From the number of milliequivalents of chromium taken, the number of milligram atoms can be found. If, in any titration, the number of milliequivalents is divided by the number of milligram atoms, the quotient is the change in valence. A milligram atom is the atomic weight of the element expressed in milligrams. The normal concentration shows the number of milliequivalents in 1 ml.

CHAPTER VI

OXIDATION AND REDUCTION: (*b*) POTASSIUM PERMANGANATE METHODS

Manganese, from the standpoint of oxidation-reduction reactions, is an interesting element. The potentials relating to the various valence states are given in the following table:

Reaction	Volts
(*a*) $\mathbf{Mn} = \mathrm{Mn}^{++} + 2e$	-1.1
(*b*) $\mathbf{MnO_2} + 4\mathrm{OH}^- = \mathrm{MnO_4}^{--} + 2\mathrm{H_2O} + 2e$	$+0.57$
(*c*) $\mathbf{MnO_2} + 4\mathrm{OH}^- = \mathrm{MnO_4}^- + 2\mathrm{H_2O} + 3e$	$+0.59$
(*d*) $\mathrm{MnO_4}^{--} = \mathrm{MnO_4}^- + e$	$+0.66$
(*e*) $\mathrm{Mn}^{+++} + 2\mathrm{H_2O} = \mathbf{MnO_2} + 4\mathrm{H}^+ + e$	$+1.2$
(*f*) $\mathrm{Mn}^{++} + 2\mathrm{H_2O} = \mathbf{MnO_2} + 4\mathrm{H}^+ + 2e$	$+1.33$
(*g*) $\mathrm{Mn}^{++} = \mathrm{Mn}^{+++} + e$	$+1.5$
(*h*) $\mathrm{Mn}^{++} + 4\mathrm{H_2O} = \mathrm{MnO_4}^- + 8\mathrm{H}^+ + 5e$	$+1.52$
(*i*) $\mathbf{MnO_2} + 2\mathrm{H_2O} = \mathrm{MnO_4}^- + 4\mathrm{H}^+ + 3e$	$+1.63$

In the table, the letter *e* signifies the electron, or the transfer of 1 faraday (96,500 coulombs) if the gram atom or gram molecule is understood. Black-faced type signifies that the substance as such is insoluble.

The formation of a manganous salt from metallic manganese is indicated by equation (*a*). The normal potential of -1.1 volts indicates that the metal is oxidized a little more easily than zinc and somewhat less readily than aluminum (which is unprotected by an oxide film). Dilute acids, therefore, dissolve the metal with the evolution of hydrogen and the formation of bivalent manganous salt. Nitric acid, aqua regia, or halogens in the presence of a strong acid are incapable of oxidizing the manganous salt. The bivalent manganous salts, although slightly colored in the form of hydrated crystals, yield colorless solutions.

Salts of trivalent manganese, called manganic salts, are known but they are not very stable. Equation (*e*) shows that it is possible under some conditions to form a manganic salt from manganese dioxide and leads one to expect that it ought to be possible to oxidize a manganic salt to manganese dioxide in the presence of alkali hydroxide or the salt of a weak acid, because, since hydrogen ions are liberated when manganic salt is oxidized, the reaction should take place more readily if the hydrogen ions are removed as fast as they are formed. The potential of reaction (*g*) in the table indicates that manganic salts are easily reduced to manganous salts.

Some salts of quadrivalent manganese are known. Thus, cold concentrated hydrochloric acid will slowly dissolve manganese dioxide, forming manganese tetrachloride. Complex salts, such as K_2MnF_6 and K_2MnCl_6, have been prepared. These salts, however, are not stable and are of little interest to the analytical chemist. The dioxide, MnO_2, occurs in nature as the mineral pyrolusite, which is the most important source of all manganese compounds and can be regarded as the anhydride of manganous acid, H_2MnO_3, which is known to have salts called manganites. The potential of reaction (*c*) in the above table indicates that it ought to be possible to form MnO_4^- from MnO_2, and conversely that MnO_2 can be expected to be formed as a reduction product when permanganate acts as an oxidizer. Potassium permanganate is much used for the oxidation of many organic compounds in neutral or alkaline solutions, and MnO_2 is the reduction product that is usually formed. The potential of reaction (*b*) shows that MnO_2 in alkaline solution should be convertible into a manganate, such as Na_2MnO_4. All manganese oxides, on being fused with caustic alkali or alkali carbonate in the air or in the presence of some oxidizing agent such as potassium nitrate, are converted into green alkali manganate, and this reaction has frequently been used as a sensitive test for manganese. Usually the precipitate of manganous hydroxide produced by adding sodium hydroxide to the solution of a manganous salt is fused with sodium carbonate on platinum, and if the melt assumes a green color, the presence of manganese is indicated. The potential of reaction (*f*) shows that manganese dioxide is a good oxidizing agent, and this corresponds to the fact that we can dissolve it by treating with acid and any good reducing agent, such as a ferrous salt, an oxalate, a sulfite, or hydrogen peroxide. With hot concentrated hydrochloric acid, chlorine is formed.

$$\mathbf{MnO_2} + 2Fe^{++} + 4H^+ = Mn^{++} + 2Fe^{+++} + 2H_2O$$
$$\mathbf{MnO_2} + C_2O_4^{--} + 4H^+ = Mn^{++} + 2CO_2 + 2H_2O$$
$$\mathbf{MnO_2} + H_2O_2 + 2H^+ = Mn^{++} + O_2 + 2H_2O$$
$$\mathbf{MnO_2} + 2HCl = MnCl_2 + Cl_2$$

Aside from its characteristic color and use as a qualitative test, the green manganate anion MnO_4^{--} is of little interest to the analytical chemist. Equations (*b*) and (*c*), however, show that the oxidation potential of the manganate anion is close to that of the permanganate anion. Sometimes, in the analysis of duplicate samples, the chemist finds after an oxidation treatment that one sample is green, showing the presence of manganate, and the other is purple owing to the formation of permanganate.

Permanganate ions, MnO_4^-, have such a strong color that a single drop of a tenth-normal permanganate solution will impart a perceptible color to 500 ml of another solution. Permanganate, therefore, is its own indicator. In most oxidations with permanganate that take place in acid solutions, the permanganate anion is reduced to colorless manganous cations and the reduction potential of the permanganate under those conditions is shown by equation (*h*) in the table on p. 107. In a nearly neutral solution, however, permanganate is capable of oxidizing manganous ions to the quadrivalent state, to which it is itself reduced. This is the so-called *Volhard* titration.

$$3Mn^{++} + 2MnO_4^- + 2H_2O = 5MnO_2 + 4H^+$$

The potential values given on p. 107 should not be regarded as absolutely accurate. The measurement of some of these potentials is difficult, and sometimes it is hard to prevent some side reaction from taking place. The work performed in any chemical reaction of oxidation-reduction can be measured in joules or watt-seconds, that is, by multiplying the quantity of electricity involved by the voltage shown. If manganese from any valence is converted into manganese at some other valence, the work performed is theoretically the same whether the oxidation takes place all at once or in several stages. This enables one to compute some of the potential values in the table on p. 107 from other values that are given. In making such computations, the signs before the voltages in the table merely indicate which direction the current is moving; it is purely arbitrary whether the signs are made positive or negative, (cf. p. 94). To show how computations can be made, the following illustration will serve:

Reaction (*f*) on p. 107 represents the oxidation of bivalent manganese to the quadrivalent state. Reaction (*i*) covers the oxidation of quadrivalent manganese to the septavalent state, and reaction (*h*) the oxidation of bivalent manganese directly to the septavalent state. In other words, reaction (*h*) represents the sum of reactions (*f*) and (*i*), and the work done is theoretically the same whether the reaction takes place in the two stages or all at once.

Energy is composed of two factors, an intensity factor and a capacity factor. The work done is measured by the product of these two factors. Thus, in measuring the work done in compressing a gas, we must take into consideration the change in volume (capacity factor) and the pressure (intensity factor), and the work done is measured by multiplying the pressure by the volume. In electrical units, the work done is measured by multiplying the amount of electricity moving (expressed in coulombs, ampere-seconds, or ampere-hours, etc.) and the potential difference (expressed in volts). In all the reactions given in the table on p. 107, therefore, the work done, or, as it is sometimes expressed, the change in the *free energy*, is proportional to the number of electrons liberated multiplied by the voltage shown. Thus in equation (*a*) the work done is proportional to the product 2 × 1.1. In the oxidation of a gram atom of manganese from the metallic to the manganous state, 2 faradays of electricity (2 × 96,500 coulombs or ampere-seconds or 2 × 26.82 ampere-hours) are involved, and the potential drop is 1.1 volt.

Then, with respect to equations (*f*), (*i*), and (*h*) in the table on p. 107, if we call the respective voltages v_1, v_2, and v_3, we have

$$2v_1 + 3v_2 = 5v_3$$

and if two of these values are known, the third can be computed. In such computations, it should be borne in mind that none of the values given in the table is to be regarded as absolutely correct. Whatever errors there may be in the values given for v_1, v_2, and v_3 are multiplied by 2, 3, and 5, respectively, so that the result of the calculation may differ a little from the value given. Thus

$$2 \times 1.33 + 3 \times 1.63 = 7.55$$

but 5 times the value given for v_3 in the table is $5 \times 1.52 = 7.60$, and this is as near as such computations can be expected to check. In this particular case, it is well to note that reaction (*h*) is the sum of reactions (*f*) and (*i*) and not the sum of reactions (*c*) and (*f*). Reaction (*c*) is very similar to reaction (*i*) but refers to a solution which is normal in OH^- whereas (*i*) refers to one which is normal in H^+.

When potassium permanganate acts as an oxidizing agent in distinctly acid solution, the manganese is reduced from a positive valence of 7 to a positive valence of 2 and the manganese atom accepts 5 electrons from the substance oxidized:

$$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O$$

The equivalent weight of potassium permanganate, or the quantity required to make 1 l of normal solution, is, therefore, one-fifth of the molecular weight. In many reactions which take place in neutral or alkaline solutions, a precipitate of manganese dioxide is formed corresponding to a reduction to the quadrivalent state, but, since a solution of potassium permanganate is usually standardized in acid solution with complete reduction of the manganese to the bivalent state, it is customary to express the normality of permanganate on this basis.

The following equations represent the action of permanganate on some of the common substances which are oxidized quantitatively by it:

$$MnO_4^- + 5Fe^{++} + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O$$
$$2MnO_4^- + 5C_2O_4^{--} + 16H^+ \rightarrow 2Mn^{++} + 10CO_2 + 8H_2O$$
$$2MnO_4^- + 5Sn^{++} + 16H^+ \rightarrow 2Mn^{++} + 5Sn^{++++} + 8H_2O$$
$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{++} + 5I_2 + 8H_2O$$
$$2MnO_4^- + 3Mn^{++} + 2H_2O \rightarrow 5\mathbf{MnO_2} + 4H^+$$
$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{++} + 8H_2O + 5O_2 \uparrow$$

Preparation of Tenth-Normal Permanganate Solution

Weigh out on a watch glass approximately 3.2 g of potassium permanganate crystals and dissolve in 1 l of water. Boil the solution 10–15 minutes, allow to stand over night, or longer, and filter through asbestos.

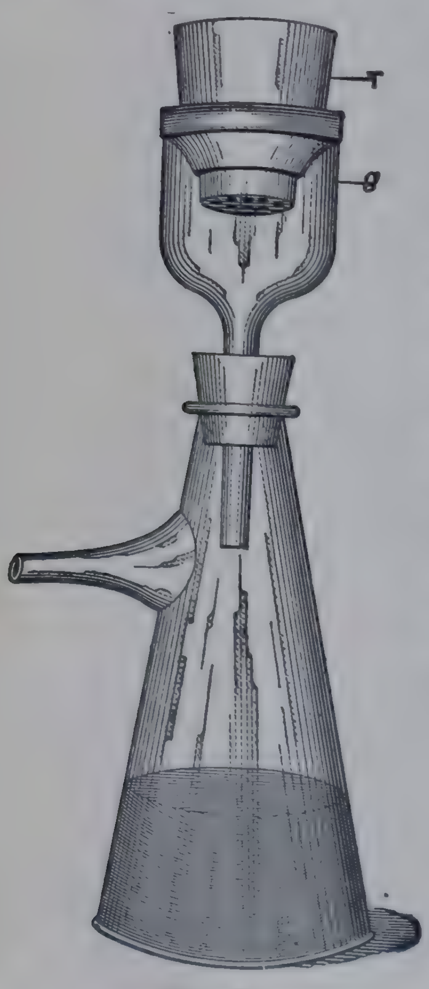

FIG. 10.

Preparation of Asbestos Filters

Cut some long-fibered, soft asbestos, of the non-hydrated variety, into pieces ½ cm long, and digest with concentrated hydrochloric acid upon the water bath for an hour. A good sample of asbestos will then be separated into very small fibers. Collect the mass in a funnel upon a filter plate, and wash with water until free from chloride. Such washed asbestos can now be purchased from dealers in chemicals.

For the preparation of a Gooch filter, shake some of the material with water in a flask, so that a thin suspension is formed. Stretch a piece of thin rubber tubing (Fig. 10) over a funnel, and place the Gooch crucible *T* in the opening. The funnel should be large enough so that the crucible is suspended by the rubber without touching the sides of the funnel. Pour enough asbestos into the crucible to produce a layer of 1- to 2-mm thickness, place a small filter plate (Fig. 11, *P*), upon this layer, and pour a little more of the

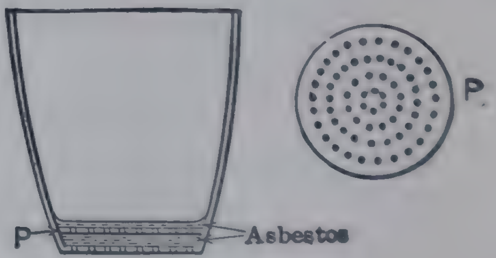

FIG. 11.

asbestos suspension into the crucible. Wash the felt with water until no asbestos fibers run through, and, in order to see them, pour the liquid into a small beaker. Usually such a filter is prepared and used with a gentle suction, but in many cases it filters more rapidly than paper without it.

For filtering the permanganate solution a thin asbestos felt on top of some glass wool in an ordinary funnel is satisfactory, and with such a filter no suction is needed. This is better than a Gooch filter, as contact of the permanganate solution with rubber will cause the formation of MnO_2, and $KMnO_4$ solution containing MnO_2 is always unstable.

The end point in a permanganate titration is easily obtained because 1 drop of the permanganate in excess imparts a distinct pink color to the solution. In permanganate work, therefore, there is not so much danger of running over the end point as with dichromate titrations and it is not necessary to have a solution on hand to titrate back with when the end point is overstepped. Many analyses, however, are accomplished by adding a measured volume of reducing agent of known strength and titrating the excess with permanganate. A solution of a ferrous salt is the commonest reducing agent thus used, but, as it oxidizes slowly on standing, its strength must be determined every day that it is used. A *pure* permanganate solution will keep indefinitely provided that it is kept in the dark, free from dust and reducing vapors. Ordinary distilled water, unless permanganate was present in the boiler, contains traces of organic material which will reduce permanganate slowly, and this is why it is well to boil the solution, let it stand some time before using it, and then filter it. Manganese dioxide is usually formed when the permanganate decomposes, and the presence of this substance serves to catalyze further decomposition so that it should be removed by filtration.

STANDARDIZATION OF PERMANGANATE SOLUTION

1. Against Sodium Oxalate (Sörensen)[1]

1000 ml of 0.1 N permanganate solution = 6.700 g $Na_2C_2O_4$

Sodium oxalate suitable for standardizing solutions can be obtained from the National Bureau of Standards at Washington, D.C. This is the most reliable standard of all those that have been proposed. Dry the sample for an hour at 130°. For the standardization Fowler and Bright[2] recommend the following procedure.

Procedure. Transfer 0.3 g of sodium oxalate (dried at 105°C) to a 600-ml beaker. Add 250 ml of diluted sulfuric acid (5 + 95)[3] previously boiled for 10 to 15 minutes and then cooled to 27 ± 3°C. Stir until the oxalate has dissolved. Add 39 to 40 ml of 0.1 *N* potassium permanganate at a rate of 25 to 35 ml per minute while stirring slowly. Let stand until the pink color disappears (about 45 seconds). Heat to 55 to 60°C, and complete the titration by adding permanganate until a faint pink color persists for 30 seconds. Add the last 0.5 to 1 ml dropwise with particular care to allow each drop to become decolorized before the next is introduced.

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[1] *Z. anal. Chem.*, **42**, 352, 512 (1903); **45**, 272 (1906).

[2] *J. Research Natl. Bur. Standards*, **15**, 493 (1935).

[3] This means 5 ml concentrated acid + 95 ml water.

Determine the excess of permanganate required to impart a pink color to the solution. This can be done by matching the color by adding permanganate to the same volume of the boiled and cooled diluted sulfuric acid at 55 to 60°C. This correction usually amounts to 0.03 to 0.05 ml.

2. Against Oxalic Acid

Owing to its water of crystallization, oxalic acid, $H_2C_2O_4 \cdot 2H_2O$ is not so reliable a standard as the sodium salt. Its equivalent weight is ½ mole = 63.03, the same as when it acts as an acid.

It is sometimes desirable to check up the oxidimetric and alkalimetric standards; oxalic acid, potassium binoxalate, or potassium tetroxalate can serve for this purpose. The method of titrating is the same as in 1. The equivalent weights of these three substances are quite similar as reducing agents but very different as acids. Thus in a liter of aqueous solution the tabulated relationships hold.

Weight per liter	Normality as Acid	Normality as Reducer
0.5 mole = 63.03 g $H_2C_2O_4 \cdot 2H_2O$	1 *N*	1 *N*
0.5 mole = 64.06 g KHC_2O_4	0.5 *N*	1 *N*
0.25 mole = 63.55 g $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$	0.75 *N*	1 *N*

3. Against Metallic Iron

It was formerly the general practice to standardize permanganate against iron wire, particularly when the standard solution was to be used for the titration of iron ores. The practice is not to be recommended because of the readiness with which the material rusts and because a low carbon content influences the results, not always in the same way. If, however, a solution of permanganate is standardized against sodium oxalate and also against iron wire, then the *apparent* iron value of the wire is known and it can be used as a standard. The method is as follows.

Weigh out 0.2 g of the wire into a 200–250-ml flask as shown in Fig. 12. Displace the air by introducing a stream of carbon dioxide, which has passed through a bottle containing water and another containing copper sulfate solution (to remove H_2S). Dissolve the wire in 55 ml of 3.6 N sulfuric acid. During the dissolving of the wire, support the flask as shown in the drawing, and with the gas-exit tube closed with a rubber stopper which is connected with a Bunsen valve.[1] Heat the contents of the flask by means of a low flame until the wire has entirely dissolved, then boil the solution gently for a short time. Allow to cool, remove the stopper, and titrate with permanganate.

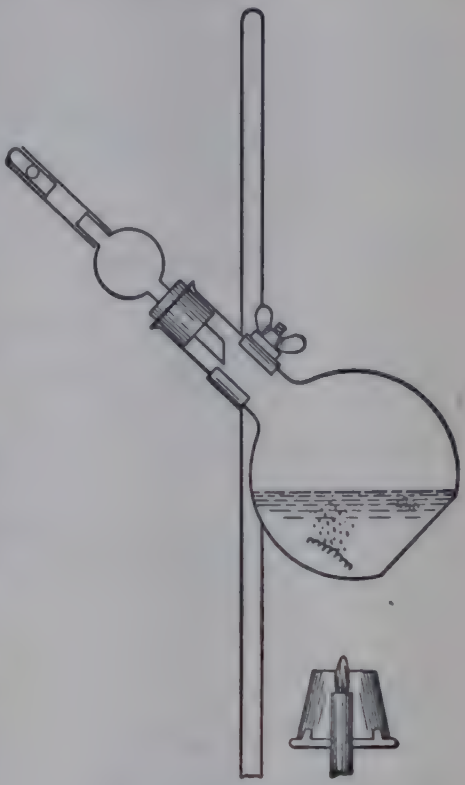

FIG. 12.

USES OF PERMANGANATE SOLUTION

1. DETERMINATION OF IRON

Method of Margueritte (1846)

$$1 \text{ ml of } 0.1\,N\ KMnO_4 \text{ corresponds to } \begin{cases} 0.005584 \text{ g Fe} \\ 0.007184 \text{ g FeO} \\ 0.007984 \text{ g } Fe_2O_3 \end{cases}$$

In this determination the iron is oxidized from the ferrous to the ferric condition:

$$MnO_4^- + 5Fe^{++} + 8H^+ \rightarrow Mn^{++} + 5Fe^{+++} + 4H_2O$$

To each 100 ml of the ferrous salt solution add 5 ml of 6 N sulfuric acid, and at a volume of about 400 ml titrate in the cold by adding potassium permanganate from a buret with glass stopcock until a permanent pink color is obtained.

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[1] A Bunsen valve consists of a short piece of rubber tubing with a cut along a few centimeters on one side, and the outer end of the tubing is closed by a glass rod. This valve prevents the entrance of air from without. A flask larger than 250-ml capacity is likely to be so thin as to break during the cooling of the iron solution. In Fig. 12, instead of a glass rod at the end of the valve, a glass tube is used which is sealed at one end and has a hole on one side. This tube serves to prevent the collapse of the rubber tubing at the place where the slit is formed.

This determination affords very accurate results and is unquestionably one of the best methods for determining iron. It, like all other procedures for titrating iron with an oxidizing solution, depends upon the preliminary reduction of any ferric iron to the ferrous state and sulfuric acid is the only permissible acid with this procedure.

Reduction of Ferric Salts to Ferrous Salts

The reduction of ferric to ferrous salts can be accomplished in a number of different ways.

1. By Hydrogen Sulfide

Saturate the solution with hydrogen sulfide and boil off the excess while introducing CO_2 into the solution which is contained in a flask.

2. By Sulfur Dioxide

Nearly neutralize the solution containing the ferric salt with sodium carbonate,[1] add an excess of sulfurous acid, boil, and pass a current of carbon dioxide through it until the excess of the reagent is completely removed.[2] Test a drop of the solution with thiocyanate to make sure that the reduction is complete; cool in an atmosphere of carbon dioxide and titrate.

3. By Metals

Metallic zinc, cadmium, or aluminum can be used to reduce ferric ions to the ferrous state. This can be done by adding small pieces of the pure metal to the ferric solution in a flask like that shown in Fig. 12 on p. 115 and heating on the water bath until the ferric solution is reduced and all the excess metal dissolved or removed by rapid filtration through a funnel containing a platinum cone. In carrying out such reductions it must be remembered that titanium, which is likely to be present in small quantities of most rocks, is reduced by these metals to the trivalent condition, whereas it is not reduced by hydrogen sulfide or sulfurous acid. Instead of pure zinc, chemists often prefer to use amalgamated zinc in a so-called *Jones reductor* (Fig. 13). The amalgamated zinc does not react with dilute sulfuric acid and liberate hydrogen but does reduce ferric sulfate solutions because, as the table of oxidation potential shows (p. 95), ferric ions are much easier to reduce than hydrogen ions.

---

[1] Ferric salts are not completely reduced by sulfurous acid in the presence of considerable hydrochloric or sulfuric acid.

[2] It is not advisable to depend upon the sense of smell. Test escaping gas from the flask by passing it through dilute sulfuric acid containing a few drops of 0.1 N $KMnO_4$ solution. If the latter is not decolorized at the end of 2 or 3 minutes, the excess of sulfurous acid has been removed.

To prepare a Jones reductor, take some 20- to 30-mesh zinc, cover with dilute hydrochloric acid, and add mercuric chloride solution while stirring up the zinc, until the evolution of hydrogen ceases. In the bottom of the reductor tube place a perforated disk or some pieces of glass, on top of this a wad of glass wool, and then just a little asbestos suspension (p. 110). If this asbestos layer is too thick, the reductor is likely to run slowly, and if too thin, some zinc powder may run through and spoil an analysis. Fill the rest of the reductor tube with the well-washed, amalgamated zinc. The use of the reductor is explained below.

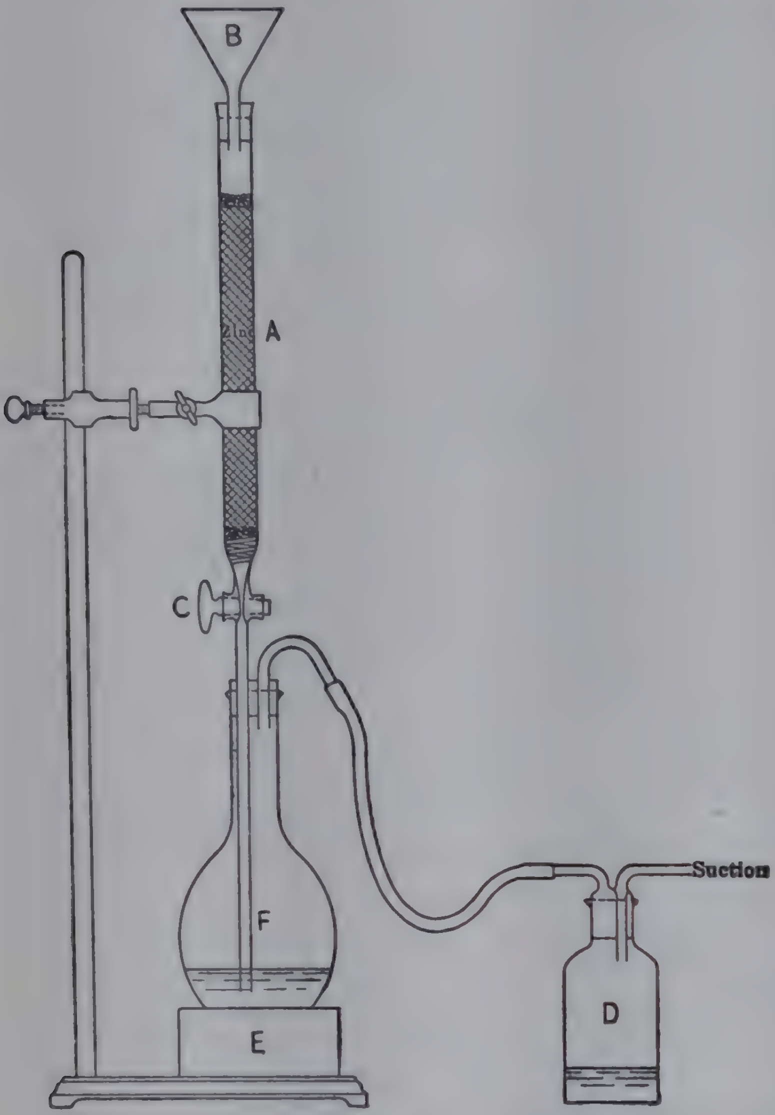

Fig. 13.

Determination of Iron in Iron Ore with the Jones Reductor

Weigh out 0.5-g samples to four significant figures and dissolve in 6 N hydrochloric acid as described on p. 104, but do not add any stannous chloride solution. To the resulting ferric chloride solution add 12 ml of 18 N sulfuric acid and evaporate, without boiling, until all hydrochloric acid has been removed, as shown by the lack of odor or by the formation of sulfuric acid fumes. Cool, dilute carefully with 100 ml of water, and run through the properly prepared reductor with which blanks have just been run. From the total volume of permanganate solution used in the analysis, deduct the volume required in the blank.

In making blanks and in all determinations, the procedure is as follows. Add 100 ml of normal sulfuric acid through the funnel *B*, with the stopcock *C* open, using a little suction. When only a little of the dilute acid remains in the funnel, add the solution to be reduced or, in the case of blanks, 50 ml of 1.5 *N* sulfuric acid, and when this has nearly passed out of the funnel, follow with 250 ml of normal sulfuric acid, washing out the original beaker with this acid and adding it in small portions. Finally, pass 100 ml of water through the reductor. At no time, however, should any air be allowed to enter the reductor tube, which should always be kept full of water when idle. Run blanks until two successive tests require less than 0.2 ml of 0.1 *N* permanganate to give a pink color to the acid solution.

4. By Stannous Chloride

This method is especially suited for metallurgical purposes, because it can be accomplished most rapidly and hydrochloric acid is the best solvent for iron ores.

Ferric chloride in hot solution is easily reduced by stannous chloride:

$$SnCl_2 + 2FeCl_3 + 2HCl = H_2SnCl_6 + 2FeCl_2$$

The complete decolorization of the solution shows the end point of reduction. The excess of stannous chloride is afterward oxidized by means of mercuric chloride:

$$SnCl_2 + 2HgCl_2 + 2HCl = H_2SnCl_6 + \mathbf{Hg_2Cl_2}$$

Requirements. • (*a*) Stannous chloride solution. Dissolve 50 g of stannous chloride in 100 ml of concentrated hydrochloric acid and dilute with water to a volume of 1 l.

(*b*) 6 *N* hydrochloric acid.

(*c*) Mercuric chloride solution. A saturated solution of the pure commercial salt in water is used.

(*d*) Manganese sulfate solution. Dissolve 67 g of crystallized manganous sulfate ($MnSO_4 \cdot 4H_2O$) in 500–600 ml of water; add 138 ml of phosphoric acid (*d* 1.7) and 130 ml of concentrated sulfuric acid; dilute the mixture to 1 l.

DETERMINATION OF IRON IN AN ORE BY THE ZIMMERMANN-REINHARDT METHOD

Procedure. Weigh out 0.25–0.3 g of the finely powdered mineral into a small beaker, add 20 ml of 6 *N* hydrochloric acid, cover the beaker with a watch glass, and heat, just below the boiling temperature, until the residue is apparently free from reddish brown mineral. Remove the flame, and add the stannous chloride solution, *drop by drop*, until the iron solution just becomes colorless, avoiding an excess. Cool to at least room temperature and add quickly 10 ml of mercuric chloride solution, whereby a slight silky precipitate of Hg_2Cl_2[1] is formed. After 5 minutes, dilute the solution to about 400 ml, add 20–25 ml of the manganese sulfate solution, and titrate the cold mixture (very slowly) with potassium permanganate until a pink color permanent for 15 seconds is obtained. Toward the last take care not to add a drop of permanganate until the color of the preceding drop has disappeared.

TITRATION OF FERROUS SALTS IN HYDROCHLORIC ACID SOLUTION

The titration of iron in hydrochloric acid solution gives high results unless particular precautions are taken. If dilute permanganate solution is allowed to run into a cold dilute solution of ferrous chloride containing hydrochloric acid, the permanganate is decolorized and the iron is oxidized, but there is noticeable evolution of chlorine.[2] More permanganate is used than is necessary to oxidize the ferrous salt to the ferric condition.

If, however, permanganate is run into cold, dilute hydrochloric acid, in the absence of ferrous salt, there is no evolution of chlorine. Furthermore, the presence of a ferric salt does not cause evolution of chlorine. The chlorine, therefore, is not a result of the direct action of the permanganate upon the hydrochloric acid, but is probably due to the oxidation of the ferrous ion to an unstable state of oxidation corresponding to a perchloride, a peroxide, ferric acid, or perferric acid.

When permanganate is run into a dilute hydrochloric acid solution containing ferrous chloride and considerable manganous salt, the ferrous iron is oxidized quantitatively to ferric iron and there is *no evolution of chlorine.* This was shown by Kessler[3] in 1863 and by Zimmermann[4] in 1881. It has since been confirmed by many other chemists.[5]

This can be explained as follows: Permanganate ions react with manganous ions to form, as Volhard[6] proved, quadrivalent manganese. In this state of oxidation, manganese is unstable in acid solution, but it is reduced more readily by ferrous ions than by chloride ions.

Zimmermann[7] suspected, and Manchot's[8] experiments confirm this view, that iron like manganese has a tendency to form unstable compounds as primary oxidation products. If such a compound is formed in the presence of manganous ions, the iron will give up its excess charge to manganous rather than to chloride ions, provided that sufficient manganous ions are present.

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[1] If the precipitate produced by mercuric chloride is at all grayish in color, the solution must be thrown away; too large an excess of stannous chloride was used. Moreover, the end point with permanganate is difficult to see if the solution contains much precipitate.

[2] Löwenthal and Lenssen, *Z. anal. Chem.*, **1863**, 329.

[3] *Pogg, Ann.*, **118**, 779, and **119**, 225.

[4] *Ber.*, **14**, 779, and *Ann. Chem. Pharm.*, **213**, 302.

[5] For example, J. A. Friend, *J. Chem. Soc.*, **95**, 1228 (1909). C. C. Jones and J. H. Jeffery, *Analyst*, **34**, 306 (1909).

[6] *Ann. Chem. Pharm.*, **198**, 337.

[7] *Ber.*, **11**, 779, and *Ann. Chem. Pharm.*, **213**, 302.

[8] *Ann. Chem. Pharm.*, **325**, 105 (1902).

According to Manchot there is a tendency in all oxidations to form an unstable compound as the primary oxidation product. When hydrogen burns in air, a little hydrogen peroxide is formed; when sodium burns, sodium peroxide results. In most cases, these primary products are unstable and cannot be isolated because of the readiness with which they are reduced to a more stable condition. When an *acceptor*[1] is present it will take up the excess charge which is lost when the primary product is reduced; in aqueous solutions in the absence of any other acceptor, free oxygen is evolved.

According to the method of oxidation, iron tends to form different primary states of oxidation. In the direct oxidation of iron by oxygen, the primary oxide appears to be FeO_2; in the oxidation by means of permanganate, chromic acid, or hydrogen peroxide, the primary oxidation product appears to contain iron with a valence of 5, whereas iron with a valence of 6 is probably formed if hypochlorous acid is the oxidizer.

According to Manchot, potassium permanganate first causes the formation of quinquevalent iron. If sufficient manganese ions are present, these play the part of acceptor, but otherwise, in hydrochloric acid solution, some chlorine is formed:

$$3\mathrm{MnO_4}^- + 5\mathrm{Fe}^{++} + 24\mathrm{H}^+ \rightarrow 3\mathrm{Mn}^{++} + 5\mathrm{Fe}^{\overset{+++}{++}} + 12\mathrm{H_2O}$$

$$\mathrm{Fe}^{\overset{+++}{++}} + \mathrm{Mn}^{++} \rightarrow \mathrm{Mn}^{\overset{++}{++}} + \mathrm{Fe}^{+++}$$

$$\mathrm{Mn}^{\overset{++}{++}} + 2\mathrm{Fe}^{++} \rightarrow \mathrm{Mn}^{++} + 2\mathrm{Fe}^{+++}$$

$$\mathrm{Fe}^{\overset{+++}{++}} + 2\mathrm{Cl}^- \rightarrow \mathrm{Cl_2} + \mathrm{Fe}^{+++}$$

The action of the manganous sulfate is partly to regulate the reaction between ferrous and permanganate ions, for, according to Volhard, the manganous ions tend to react with permanganate, thus slowing down the reaction between permanganate and ferrous ions. The quadrivalent manganese formed by the action of permanganate on manganous ions at once reacts with ferrous ions; the manganous ions also act as acceptor toward any iron oxidized above the trivalent state. In both cases it is essential that manganese peroxide does not react with hydrochloric acid very rapidly, and it is necessary, too, that the amount of manganous salt shall greatly exceed the amount of iron present.

Although it is possible, then, to titrate iron in hydrochloric acid solutions in the presence of manganous sulfate, the method possesses the disadvantage that the end point cannot be seen so distinctly as when no chloride is present, since ferric chloride forms a much more yellow solution than does ferric sulfate. This difficulty is overcome by the addition of phosphoric acid as suggested by C. Reinhardt. The titration in hydrochloric acid in the presence of manganese sulfate and phosphoric acid is called the Zimmermann-Reinhardt method (cf. p. 116).

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[1] An *acceptor* is a substance which is not oxidized by oxygen alone, but can be oxidized by the aid of some other substance present called an *auto-oxidator*. A substance which tends to be peroxidized may play the part of an acceptor. Cf. Engler, *Ber.*, **33**, 1097 (1900).

2. DETERMINATION OF MANGANESE DIOXIDE IN PYROLUSITE

This is an indirect analysis like that of chromite described on p. 104. The sample is dissolved by treating it with sulfuric acid and a suitable reducing agent, such as ferrous sulfate solution or oxalic acid, and the excess of reducing agent is finally determined by titrating with permanganate.

$$\mathrm{MnO_2 + 2Fe^{++} + 4H^+ \rightarrow Mn^{++} + 2Fe^{+++} + 2H_2O}$$

or

$$\mathrm{MnO_2 + C_2O_4^{--} + 4H^+ \rightarrow Mn^{++} + 2CO_2 + 2H_2O}$$

For each analysis, weigh out portions of the finely ground ore, which has been dried to constant weight at 120°, into 300-ml Erlenmeyer flasks, using samples that do not vary more than 0.05 g from 0.45 g. Add to each portion of ore a carefully weighed portion of pure sodium oxalate, using at least one and one-half times as much oxalate as pyrolusite but not more than 0.8 g in any case. Add 50 ml of water and 50 ml of 6 N sulfuric acid and heat, without boiling hard, until no more pyrolusite remains undissolved. Keep the flasks covered with watch glasses, and do not allow the solutions to evaporate to less than 85 ml, adding hot water from time to time if necessary. When all the black ore has dissolved, dilute to 200 ml and titrate with 0.1 N permanganate, keeping the solution above 60°.

If s is the weight of pyrolusite used, r the weight of sodium oxalate, and n the milliliters of N normal permanganate required for the excess oxalate,

$$\left(\frac{r}{0.067 \times N} - n\right)\frac{N \times 0.0435 \times 100}{s} = \text{per cent of } \mathrm{MnO_2}$$

In this equation, 0.067 is the equivalent weight of sodium oxalate and 0.0435 the equivalent weight of manganese dioxide.

HOME PROBLEMS

50. After being dissolved and reduced, 0.2186 g of an ore reacted with 25.14 ml of 0.0996 N $\mathrm{KMnO_4}$ solution. Find percentage of Fe and of $\mathrm{Fe_2O_3}$, assuming all the Fe to be present in the latter state.

51. What weight of limonite should be taken with this last permanganate so that each milliliter indicates 2 per cent of Fe?

52. Using the same solution, find the maximum weight of 70 per cent Fe ore that can be titrated without refilling a 50-ml buret.

53. Given two permanganate solutions. Solution A contains 15.07 mg of $\mathrm{KMnO_4}$ per milliliter, and 20 ml of solution B react with 0.12 g of ferrous Fe. In what proportions should the solutions be mixed so that the resulting solution will be $N/3$ without dilution?

54. If 50 ml of either of the above solutions is reduced to manganous salt and then titrated by the Volhard method with the same $KMnO_4$ solution, how many milliliters will be required?

55. Find the percentage of Pb_3O_4 in a sample of red lead if 2.5 g is treated with 50 ml of K tetroxalate solution which is 0.15 N as an acid and the excess requires 30.00 ml of $KMnO_4$ of which 1 ml oxidizes 0.005584 g of Fe by the Margueritte method.

$$Pb_3O_4 + C_2O_4^{--} + 8H^+ \rightarrow 3Pb^{++} + 4H_2O + 2CO_2 \uparrow$$

56. What weights of MnO_2 ore and of pure oxalic acid $H_2C_2O_4{\cdot}2H_2O$ should be used in the pyrolusite analysis so that the percentage of MnO_2 will be obtained by subtracting the milliliters of 0.14 N $KMnO_4$ used from 150?

Hint. In this problem, every milliliter of $KMnO_4$ solution used is equivalent in oxidizing power to a quantity of MnO_2 which represents 1 per cent of the weight of the ore taken for analysis. The number 150 must represent the volume of permanganate solution required to oxidize the entire weight of oxalic acid used; in other words, in the formula given for the computation of the pyrolusite analysis, $r/(0.063 \times N) = 150$, using the equivalent weight of oxalic acid rather than that of sodium oxalate.

57. Find the number corresponding to 150 in the last problem and the normality of the $KMnO_4$ when the same result is obtained with 0.48 g of pyrolusite and 0.84 g of oxalic acid.

58. Using sufficient oxalate to react with all the MnO_2, what weight of pyrolusite and what normality of $KMnO_4$ should be used so that $100r - n =$ per cent MnO_2, when r is the weight of oxalic acid crystals and n is the volume of $KMnO_4$ required for the excess oxalic acid? (Note that $100r$ must be the number of milliliters of $KMnO_4$ which are equivalent to r g of $H_2C_2O_4{\cdot}2H_2O$.)

59. What volume of O_2 will be liberated at 23° and 750 mm pressure when 30 ml of 0.09 N $KMnO_4$ reacts with an equivalent quantity of H_2O_2 solution

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{++} + 8H_2O + 5O_2 \uparrow$$

1 mole of O_2 = 22.4 l at 0° and 760 mm. pressure.

60. The calcium in a sample of limestone is determined by precipitation as CaC_2O_4, the precipitate being dissolved in acid and the oxalic acid being titrated with permanganate. What weight of sample should be taken for analysis such that the milliliters of 0.12 N $KMnO_4$ will be the same number as the percentage of CaO in the sample?

61. What volume of 0.09 N $KMnO_4$ will react with 9 ml of H_2O_2 solution, d 1.04, containing 3.04 per cent H_2O_2 by weight and what volume of O_2 will be evolved at 750 mm and 20° as a result of the reaction?

62. In the analysis of pyrolusite, a sample weighing 0.3216 g is dissolved in sulfuric acid in the presence of 50.00 ml of 0.1100 N ferrous solution. The excess ferrous ion is titrated with 11.25 ml of 0.1200 N $KMnO_4$. Calculate (*a*) the percentage of MnO_2 and (*b*) the percentage of *available* oxygen (in this analysis one molecule of MnO_2 is assumed to furnish one atom of available oxygen).

63. Under proper conditions, antimony can be oxidized from the trivalent to quinquevalent state by permanganate. A sample of antimony ore was titrated with 25.25 ml of 0.1045 N $KMnO_4$. Find the percentage of Sb present.

CHAPTER VII

OXIDATION AND REDUCTION: (*c*) CERIC SULFATE METHOD OXIDATION-REDUCTION INDICATORS

Cerium forms colorless cerous salts in which it has a valence of 3 and yellow or orange ceric salts in which it has a valence of 4. Cerous salts can be oxidized to ceric salts in acid solutions (*a*) by heating with lead dioxide and 5 N nitric acid, (*b*) by heating with ammonium persulfate, (*c*) by electrolysis, and (*d*) by sodium bismuthate.

$$2Ce^{+++} + PbO_2 + 4H^+ = 2Ce^{++++} + Pb^{++} + 2H_2O$$

$$2Ce^{+++} + S_2O_8^{--} = 2Ce^{++++} + 2SO_4^{--}$$

$$Ce^{+++} = Ce^{++++} + e$$

$$2Ce^{+++} + NaBiO_3 + 6H^+ = 2Ce^{++++} + Na^+ + Bi^{+++} + 3H_2O$$

As a result of the oxidation, the colorless cerous solution becomes yellow or orange. If a solution of a cerous salt is treated with an excess of alkali hydroxide and chlorine gas is led through the solution, the white cerous hydroxide, $Ce(OH)_3$, which forms when the solution is made basic, is changed to light yellow ceric hydroxide, $Ce(OH)_4$. The precipitate of ceric hydroxide dissolves in nitric acid yielding a red solution, but when acted upon by hydrochloric acid, colorless cerous chloride is formed and chlorine is evolved as a result of the oxidation of some of the hydrogen chloride.

The normal potential corresponding to the reaction $Ce^{+++} = Ce^{++++} + e$ is +1.45 volts. If we compare this with the reaction $Mn^{++} + 4H_2O = MnO_4^- + 8H^+ + 5e$ which has a normal potential of +1.52 volts and with the reaction $2Cr^{+++} + 7H_2O = Cr_2O_7^{--} + 6e$ which has a normal potential of +1.3 volts, we see that ceric sulfate is a stronger oxidizing agent than potassium dichromate and is nearly as strong as potassium permanganate. Ceric sulfate solutions are less sensitive to hydrochloric acid than are solutions of potassium permanganate, and there is but one possible reduction product. The oxidation potential varies with the character of the anion present. The above value 1.45 holds in sulfate solutions. It is 1.28 in chloride solutions, 1.61 in the presence of nitrate, and 1.70 for perchlorate. A possible explanation is that the ceric ion is not present as such but in the form of a complex ion.

Were it not for the fact that ceric salts are much more expensive than equivalent quantities of permanganate, doubtless the use of these salts as oxidation agents would be far more prevalent. On the other hand, the cost of the reagent is by no means prohibitive, and it is already being used widely. Like permanganate and unlike potassium dichromate, the ceric salt is not suitable for use as a primary standard or, in other words, a standard solution cannot be obtained by weighing out an exact quantity of the reagent.[1] The reagent should be prepared by dissolving approximately the proper quantity of ceric salt, and the solution should then be standardized by titration against sodium oxalate or a solution containing ferrous salt.

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[1] The compound $(NH_4)_2Ce(NO_3)_6$ has been recommended as a suitable standard in oxidimetry. Smith, Sullivan, and Frank, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 449 (1936).

Ceric solutions, like those of potassium permanganate, can serve as their own indicators for the titration of colorless solutions, but the color change is not so marked and it requires a little more of the ceric solution to impart a perceptible tint to the fully titrated solution. The color change is more noticeable in hot solutions than in the cold. In the titration of ferrous salts with ceric sulfate it is best to add phosphoric acid to form the colorless ferric acid phosphate complex and to use ferrous orthophenanthroline as indicator. Diphenylamine, sulfonic acid, diphenylbenzidine, and some similar organic compounds can also be used as indicators. These indicators form oxidation products which have colors easily distinguishable from the colors of the unoxidized compounds, and the oxidation-reduction potential is such that the organic compound is not oxidized until after practically all the substance being titrated has entered into the reaction; in other words, the color change takes place when the desired oxidation of the substance being analyzed has been completed.

In some reactions which take place readily with permanganate, a catalyst must be used with ceric solution. Thus the titration of oxalate is best accomplished with iodine monochloride, ICl, as catalyst, and the oxidation of arsenite can be catalyzed with OsO_4.

To prepare the iodine monochloride solution, dissolve 0.1395 g KIO_3 and 0.0890 g KI in 125 ml of water and at once add 125 ml of concentrated HCl. Cool to room temperature, add 5 ml of $CHCl_3$, and titrate carefully either with 0.1 N KIO_3 or KI until the chloroform layer shows only a very faint iodine after vigorous shaking in a glass-stoppered bottle. For 100 ml of solution to be titrated with $Ce(SO_4)_2$, add 2.5 ml of this solution and 1 drop of ferrous phenanthroline indicator solution. Diphenylamine sulfonate indicator can also be used.

Preparation of 0.1 N Ceric Sulfate Solution[1]

Ceric sulfate solutions can be prepared by digesting the oxide, CeO_2, with strong sulfuric acid at 125° or higher, cooling, and diluting. The solution after being diluted should be 1–2 N in sulfuric acid. Ceric oxide of suitable purity can be purchased as such, or it may be made by igniting cerous oxalate, which is one of the cheapest cerium salts, to 600–625° for about 10 hours.

It is far more convenient to use pure ceric ammonium sulfate, $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$, which can be purchased from dealers in chemicals and has the high molecular weight of 632.5. Weigh out approximately 65 g of the salt, add 500 ml of 2 N sulfuric acid, and stir till all the solid has dissolved. Dilute to about 1 l, mix well, and keep in a glass-stoppered bottle.

Standardization. Sodium oxalate, arsenic trioxide, or iron wire can be used for standardization. The reactions with oxalate and trivalent arsenic are slow, and the presence of a catalyst is desirable. For this purpose a little iodine monochloride is recommended for the oxalate titration and some osmium tetroxide, OsO_4, for the arsenite (3 drops of a solution obtained by dissolving 0.25 g OsO_4 in 100 ml of 0.1 *N* H_2SO_4).

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[1] Willard and Young, *J. Am. Chem. Soc.*, **50**, 1322, 1334, 1372 (1918). Willard and Furman, *Elementary Quantitative Analysis*.

(*a*) *Against Arsenic Trioxide.* Weigh out 0.15–0.22 g of pure As_2O_3 into a 250-ml Erlenmeyer flask, add 15 ml of 2 *N* NaOH, and heat gently to hasten the dissolving. When all the white powder has dissolved, cool to room temperature; add 25 ml of 6 *N* H_2SO_4, 3 drops of 0.01 *M* OsO_4 solution (see above), and 1 or 2 drops of ferrous phenanthroline indicator (1.5 g of *o*-phenanthroline monohydrate in 100 ml of freshly prepared 0.025 *M* ferrous sulfate solution). Titrate with approximately 0.1 *N* ceric ammonium sulfate solution until the reddish orange color of the indicator changes to colorless or very pale blue.

(*b*) *Against Pure Iron.* Weigh out accurately duplicate portions of about 0.25 g of iron wire (specially prepared for standardization) into 100-ml beakers; add to each 5 ml of water and 10 ml of concentrated hydrochloric acid. Heat gently until all the metal has dissolved. Unless particular precautions are taken to avoid oxidation (see p. 113) the solution will show a slight yellow color, due to the formation of a little ferric chloride as a result of atmospheric oxidation; hydrochloric acid alone can only oxidize iron to the ferrous state. To convert all the iron to the ferrous condition, carefully add stannous chloride solution (see p. 116) until the hot solution no longer shows any yellow color, but avoid adding an excess of the reagent. Cool by placing the beaker in running water, transfer to a 400-ml beaker, dilute to 150 ml, and add 10 ml of mercuric chloride solution (cf. p. 116). A white, silky precipitate of mercurous chloride should be formed. If the precipitate is dark in color or is bulky, it is best to throw the solution away and start again. To the ferrous solution add 10 ml of phosphoric acid, *d* 1.37, and 0.3 ml of 0.01 *M* diphenylamine sodium sulfonate. (To prepare this indicator solution, dissolve 0.32 g of the barium salt in 100 ml of water, add 0.5 g of solid sodium sulfate, stir well, and allow the barium sulfate precipitate to settle. Decant off the clear solution.) One or two drops of ferrous *o*-phenanthroline indicator solution can be used instead of the diphenylamine sulfonate. Titrate with the ceric sulfate solution until the solution assumes a distinct purple tint. The reaction between the indicator and the ceric sulfate is rapid but not instantaneous; the reagent should be added slowly toward the last.

$$Fe^{++} + Ce^{++++} \rightarrow Fe^{+++} + Ce^{+++}$$

Determination of Iron in an Iron Ore

Dissolve 0.25–0.30 g of the powdered ore by heating gently with 20 ml of 6 *N* hydrochloric acid exactly as described on p. 116. After the reduction with stannous chloride and treatment with mercuric chloride, add 10 ml of phosphoric acid, *d* 1.37, and 0.3 ml of 0.01 *M* diphenylamine sodium sulfonate indicator solution. Titrate with ceric sulfate solution as just described for the standardization of the solution against pure iron.

Ceric sulfate can be used for many other oxidations. It oxidizes hydrogen peroxide, nitrous acid, hydrazine, hydroxylamine, hydrazoic acid, tartaric acid, oxalic acid, anthracene, sodium thiosulfate, sulfurous acid, and hypophosphorous acid as well as many other substances. Some of these reactions can be utilized for various titrations. Thus the oxidation of the oxalate ion can be used not alone for standardizing the ceric solution but also for determining cations like calcium, strontium, and lead which form insoluble oxalates. All the filtered precipitates yield oxalic acid, when digested with dilute acid, and the oxalic acid can be titrated with ceric sulfate.

Oxidation-Reduction Indicators

In the chapters on potassium dichromate and ceric sulfate methods, the use of oxidation-reduction indicators (or *redox* indicators, as they are sometimes called) was advocated. Their action is in many respects comparable to that of acid-base indicators. The oxidation-reduction indicators are organic compounds which change color when oxidized or reduced. This change in color takes place at definite oxidation potentials. The indicator reaction can be expressed by the reversible equation

$$I_{\mathrm{Ox}} + ne \rightleftarrows I_{\mathrm{Red}}$$

where I_{Ox} represents the oxidized form and I_{Red} is the reduced form. The action of the indicator does not depend upon the specific nature of the oxidant or reductant but upon the relative oxidation potentials of the indicator and of the system titrated. Thus, for titrations of a ferrous salt with ceric sulfate, the indicator used should be chosen so that the indicator will not change color until all the ferrous salt has been oxidized, and the oxidation potential of the indicator reaction must lie between that of the ceric sulfate and that of the ferrous solutions. The oxidation-reduction indicators which are most used in common titrations are diphenylamine, diphenylbenzidine, diphenylamine sulfonic acid, and phenanthroline-ferrous ion. Quite a number of other substances have been proposed and are now being studied.

Diphenylamine and diphenylbenzidine have been used widely. Both these compounds are sparingly soluble in water, and the indicator solutions are prepared by dissolving 1 g in 100 ml of concentrated sulfuric acid. A few drops of either solution suffices for a titration in a volume of 200–300 ml. Upon oxidation, diphenylamine, $C_6H_5 \cdot NH \cdot C_6H_5$, is changed to diphenylbenzidine, $(C_6H_5 \cdot NH \cdot C_6H_4)_2$. This reaction is not reversible, and both substances are colorless. Diphenylbenzidine is oxidized to a violet oxidation product called diphenylbenzidine violet,

$$C_6H_5{\cdot}N{:}C_6H_4{:}C_6H_4{:}N{\cdot}C_6H_5$$

The normal oxidation potential of this reaction is +0.76 volt. These indicators can be used in titrations with permanganate, ceric sulfate, dichromate, and vanadate against ferrous sulfate, but the diphenylbenzidine violet is not stable toward oxidizing agents and is slowly but irreversibly oxidized further. The slight solubilities in water and the fact that they cannot be used in the presence of tungstate are handicaps. On the other hand, diphenylamine sulfonate is much more soluble in water and can be used in the presence of tungstate.

Diphenylamine sulfonic acid (cf. p. 101) gives a green color with ferrous salts which is probably caused by a combination of unoxidized diphenylamine sulfonic acid with some of the violet oxidation product. The violet color does not appear until all ferrous salt is oxidized. The oxidation of the indicator requires an appreciable quantity of 0.01 *N* oxidant, but the indicator correction is small in the case of 0.1 *N* solutions. The color change in titrating ferrous salts is sharp, but the reddish oxidation product is slowly decomposed on standing and the tint does not increase upon addition of excess oxidant. The color change is explained as in the case of diphenylbenzidine (see above).

Phenanthroline-Ferrous Ion. The organic base *o*-phenanthroline, $C_{12}H_8N_2$, dissolves easily in solutions of ferrous salts forming a red complex cation $Fe(C_{12}H_8N_2)_3^{++}$ of an intensely red color; strong oxidizing agents convert this ion to pale blue $Fe(C_{12}H_8N_2)_3^{+++}$. The ferrous complex is decomposed slowly by strong acids or by salts of Co^{++}, Cu^{++}, Ni^{++}, Zn^{++}, or Cd^{++} which also form complexes with phenanthroline. The blue oxidized form resists further oxidizing action. The color change of red to blue is reversible. To prepare the indicator solution dissolve 1.48 g of *o*-phenanthroline in 100 ml of 0.025 *N* ferrous sulfate solution. The indicator can also be purchased under the name *Ferroin*. The color change takes place when 90 per cent of the indicator has been oxidized and the oxidation potential is about 1.20 volts, which is much higher than in the case of the above-mentioned indicators. This indicator is very useful in titrations with ceric sulfate of solutions containing ferrous iron, ferrocyanide, vanadyl salt, etc., but with dichromate titrations the diphenylamine sulfonate is better. The present cost of *o*-phenanthroline is about $2.00 a gram.

HOME PROBLEMS

64. Compute the cost for making 30 l of 0.12 *N* cerium sulfate solution: (*a*) starting with $CeCO_3$ at $5 per kilogram, assuming that this is first converted into CeO_2 by ignition in the air and neglecting the cost of the sulfuric acid, water, labor and fuel; (*b*) starting with pure CeO_2 at $4 per kilogram; and (*c*) starting with ceric ammonium sulfate at $1 per kilogram.

65. Compute the cost of making 30 l of 0.12 *N* potassium dichromate solution assuming that the pure dichromate costs 12 cents a pound and for making the same quantity of 0.1 *N* potassium permanganate solution if the reagent costs 25 cents a pound.

66. Compute the percentage of Fe_2O_3 in an iron ore from the following data: 0.28 g of the ore required 24 ml of ceric sulfate solution after dissolving the sample in hydrochloric acid and reducing with stannous chloride; 38 ml of the ceric solution

oxidized 0.22 g of pure iron. In all the titrations, an excess of 0.04 ml of the ceric solution was required to impart the proper tint at the end point.

67. Calculate the CaO content of a limestone of which a sample weighing 0.60 g yielded a calcium oxalate precipitate which was equivalent to 48.0 ml of 0.08 *N* ceric sulfate solution.

68. What would be a suitable normal potential for titrating a solution containing 0.5935 g Sn with ceric sulfate solution when the final volume is 200 ml?

69. If the monohydrate of *o*-phenanthroline costs $2 a gram and ceric ammonium sulfate costs $1.00 per kg, calculate the cost of oxidant and of indicator for the laboratory work of a class of 30 students on the assumption that each student will make up 500 ml of 0.1 *N* ceric solution and use 1.00 ml of the indicator solution containing 1.48 g of *o*-phenanthroline in 100 ml.

CHAPTER VIII

OXIDATION AND REDUCTION: (*d*) IODIMETRY

ANALYSIS OF STIBNITE, COPPER ORE, SULFIDES, ETC.

The fundamental reaction of iodimetry is the following:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

or

$$2S_2O_3^{--} + I_2 \rightarrow 2I^- + S_4O_6^{--}$$

If to a solution containing a little iodine some starch solution is added, and sodium thiosulfate solution is run in from a buret, the blue color of the iodo-starch will disappear from the solution as soon as all the iodine has been reduced to iodide in accordance with the above equation. This is one of the most sensitive reactions used in analytical chemistry. If, therefore, a sodium thiosulfate solution of known strength is at hand, we have a means of determining not only iodine itself, but all those substances (oxidizing agents) which when treated with potassium iodide set iodine free, or when acted upon by hydrochloric acid evolve chlorine. Consequently, iodimetric processes are not only accurate but also capable of most general application.

Under iodimetry two kinds of methods are studied: (*a*) *direct methods*, in which iodine solution is used as the reagent and the end point is the blue color imparted to starch as soon as 1 drop of the reagent in excess has been added; and (*b*) *indirect methods*, in which an acid solution of some oxidizing agent is treated with an excess of potassium iodide and iodine equivalent to the quantity of oxidizer present is liberated. In the direct methods, iodine is used as an oxidizing agent; in the indirect methods hydriodic acid is used as a reducing agent. Iodimetric methods have, therefore, been applied to numerous reactions of oxidation and reduction. As a rule, these methods are sensitive and accurate. Direct iodimetric methods are the oxidation of sulfurous acid to sulfuric acid, of hydrogen sulfide to free sulfur, of stannous chloride to stannic chloride, of arsenite to arsenate in a solution kept nearly neutral, and of trivalent antimony salt to the quinquevalent condition in a neutral solution. Indirect methods in which iodine equivalent to the substance analyzed is liberated by adding an excess of potassium iodide to the acid solution are illustrated by the determinations of bromine, chlorine, iodate, periodate, hypobromite, bromate, hypochlorite, chlorite, chlorate, persulfate, permanganate, hydrogen peroxide, nitrite, arsenate in strongly acid solutions, ferricyanide, chromate, permanganate, manganese dioxide, lead dioxide, minium or red lead, ferric ions, cupric ions, and antimonate ions.

The words *iodimetric* and *iodometric* have been used more or less indiscriminately by chemists. Thus, of thirteen textbooks selected at random, the former spelling is preferred in nine, and the latter spelling in four. In the excellent work of Kolthoff and Sandell, however, a distinction is made and iodimetric procedures are defined as those in which iodine solution is used as oxidant and iodometric methods as those in which iodine is liberated and the final titration is made with thiosulfate. It is not at all unreasonable to make such a distinction, and perhaps in the future it will be made more generally. In this book, as the above paragraph shows, there is no attempt to make such a distinction, and the term *iodimetric* is used to cover both types of reactions. In the second edition, the other spelling was used.

The potential of the normal iodine/iodide system is +0.535 volt, which shows that iodine is a much weaker oxidizing agent than permanganate, ceric salt, or dichromate. Its potential does not depend upon the acidity of the solution, but the normal potentials of anions such as permanganate, dichromate, arsenate, antimonate, etc., do to a marked degree. For example, it is possible to oxidize arsenic quantitatively by iodine from the trivalent to the quinquevalent state if the pH is kept between 4 and 9, but in the presence of considerable hydrochloric acid the reduction from the quinquevalent to trivalent state takes place completely upon the addition of an excess of potassium iodide.

The end point in iodimetric processes is usually determined by the blue color of starch iodide which is formed when starch is present as soon as a very slight excess of iodine is present. In making titrations with iodine, therefore, starch can be added at the start and the approach of the end point will be shown by the formation of a dark blue color when the drop of iodine touches the solution but the color fades as the solution is stirred. At the end point, the color will not fade. In the indirect titrations, on the other hand, the starch should not be added until toward the end of the titration, when the presence of free iodine is not clearly shown by the lack of brown color.

Instead of starch, many chemists prefer to use carbon tetrachloride. One liter of pure water will dissolve only about 0.32 g of pure iodine, but the same quantity of CCl_4 will dissolve over 30 g of it. Iodine, therefore, is about 100 times as soluble in the CCl_4 as it is in water, and the CCl_4 solution is very highly colored. When CCl_4 is added to a water solution it falls to the bottom of the vessel and does not dissolve appreciably. If the water contains a little dissolved iodine, then, on shaking the greater part of the iodine will dissolve in the CCl_4, because of its greater solubility in it, and the color of the few drops of CCl_4 will be very much deeper than that of the original aqueous solution. Indirect iodimetric titrations are, therefore, often made in a 250-ml glass-stoppered bottle. After adding the excess of potassium iodide, a little carbon tetrachloride is added and the titration with sodium thiosulfate is begun. At first the presence of iodine in the aqueous solution will be apparent, and gentle rotation of the liquid causes sufficient mixing. Toward the end of the titration, the bottle is stoppered and shaken after each addition of sodium thiosulfate, and the end point is when the CCl_4 solution becomes colorless. In the distribution of a substance between two immiscible solvents, the ratio of the concentrations remains constant for a given molecular species. Therefore, as soon as some of the iodine is reduced in the aqueous layer by means of the thiosulfate, some of the iodine will pass from the CCl_4 to the water. Shaking the mixture helps to establish the equilibrium by breaking up the CCl_4 bubble and forcing it through all parts of the aqueous solution. This method is more sensitive than the determination of the end point with starch.

It was stated above that only about 0.32 g of iodine will dissolve in a liter of water. This corresponds to a normal concentration of 0.0025. In aqueous potassium iodide solution, the solubility is increased greatly; thus by adding 65 g of KI to a liter of water as much as 35 g of iodine will dissolve, which corresponds to a normal concentration of 0.275, and if 100 g of KI is present in 200 ml of water 153 g of iodine will dissolve. In such solutions, the following reaction takes place to a considerable extent:

$$I_2 + I^- \rightarrow I_3^-$$

The reaction constant for this equilibrium has the high value of 770. The vapor pressure of the iodine from the aqueous solution is lowered by the formation of the triiodide anion, and yet the solution as a reagent behaves exactly like free iodine. To a considerable extent the potassium iodide interferes with the dissolving out of the iodine by another solvent such as CCl_4 but not enough to prevent the determination of the end point as indicated above.

The Starch Solution

Triturate 0.5 g of *soluble starch* with a little cold water to a thin paste, and rinse this into 25 ml of boiling water; pour this into 25 ml of boiling water and boil about 2 minutes. Cool, and add 1.0 g of KI. Use 0.5 ml for each 100 ml of solution.

Sensitiveness of the Iodo-Starch Reaction

Iodine produces a blue color with starch only when hydriodic acid or a soluble iodide is present, and further, the formation of the blue color not only depends upon the presence of iodide but also is largely influenced by the concentration of the iodide solution. With the same amount of iodide and different volumes of liquid quite different amounts of iodine are necessary to produce the blue color. From this it is evident that in any iodimetric analysis about the same concentration should be maintained as in the standardization of the solutions used for the analysis. When 0.1 *N* solutions are used, the error produced by not following this rule is a small one and for most purposes can be neglected. On the other hand, when an analysis is made with 0.01 *N* solutions, a large error may be introduced and a blank should always be made to determine how much iodine solution is required to give an end point. The results of a series of experiments show that the amount of iodine solution necessary to produce the blue color in the absence of potassium iodide is directly proportioned to the dilution. If the solution contains 1 g of potassium iodide, a blue color will be produced by the same amount of iodine solution as long as not more than 150 ml of solution is present, but with a greater volume than that, more iodine is necessary irrespective of whether the solution contains 1 g or more of potassium iodide.

Preparation of Sodium Thiosulfate Solution

From the equation on p. 127 it is evident that an equivalent weight of iodine, the atomic weight in grams, is equal to 1 mole of $Na_2S_2O_3$. Hence, exactly 0.1 mole of crystallized sodium thiosulfate ($Na_2S_2O_3 + 5H_2O$) is required to make 1 l of tenth-normal solution.

A solution of pure sodium thiosulfate in doubly distilled water will keep very well, but thiosulfate solutions usually deposit sulfur on standing and the titer changes until the decomposition brought about by impurities is complete. The principal cause of the decomposition is bacterial action. Sterile solutions, free from carbon dioxide, keep indefinitely. The addition of about 3.8 g of borax per liter helps to keep the solution sterile, but the solution should be filtered if turbid.

Prepare the thiosulfate solution by dissolving the required amount of the commercial salt in freshly boiled water containing a little borax. If convenient, it is well to let the solution stand a week or so before determining its exact concentration.

The molecular weight of $Na_2S_2O_3 \cdot 5H_2O$ is 248.19. To prepare 1 l of 0.1 *N* solution 24.83 g of the salt are necessary, or, in round numbers, 25 g.

Standardization of Sodium Thiosulfate Solution

1. *With Copper Wire*

In technical work it is customary to standardize the thiosulfate solution against pure copper. Weigh out 0.2 g of pure copper wire into a 200-ml Erlenmeyer flask and dissolve in 5 ml of 8 *N* HNO_3. Dilute with 25 ml of water, boil a minute to remove oxides of nitrogen, and add 1 g of urea. Remove the flask from the flame and add strong ammonia until a white precipitate begins to form; if a permanent blue color is produced, boil off the excess ammonia. Add 7 ml of glacial acetic acid or 20 ml of 6 *N* acetic acid, which dissolves any precipitate or copper oxide that has formed. Cool to room temperature, add 3 g of potassium iodide, and titrate the brown solution with sodium thiosulfate until nearly colorless, than add starch solution, and complete the titration. In making the titration for the first time, one is bothered somewhat by the fact that the cuprous iodide is usually colored a little by adsorbed iodo-starch and is not a pure white at the end point. If t ml of the thiosulfate solution were used in titrating a g of copper, then 1 ml of thiosulfate = a/t grams Cu and the thiosulfate solution is $a/(t \times 0.06357)$

normal. The reactions that take place can be expressed as follows:

$$3\mathbf{Cu} + 8H^+ + 2NO_3^- \rightarrow 3Cu^{++} + 4H_2O + 2NO \uparrow$$
$$HNO_2 + Br_2 + H_2O \rightarrow HNO_3 + 2HBr$$
$$Cu^{++} + 4NH_3 \rightarrow Cu(NH_3)_4^{++}$$
$$Cu(NH_3)_4^{++} + 4HC_2H_3O_2 \rightarrow Cu^{++} + 4NH_4^+ + 4C_2H_3O_2^-$$
$$2Cu^{++} + 4I^- \rightarrow \mathbf{Cu_2I_2} + I_2$$
$$I_2 + 2S_2O_3^{--} \rightarrow 2I^- + S_4O_6^{--}$$

Although 4 molecules of iodide react with 2 of copper, only 1 molecule of iodine is liberated. The equivalent weight of copper, therefore, corresponds to the reduction of *bivalent* copper to *univalent* copper and is the atomic weight of copper.

Note: The precipitate of cuprous iodide is usually colored pink at the end point because of adsorbed iodine, and this iodine slowly comes back into solution to give a fading end point. The addition of 2 g KCNS or NH_4CNS (dissolved in 10 ml of water) a little before the end point is reached, when the starch indicator solution is to be added, will serve to displace the iodine adsorbed on the surface of the precipitate and give a better end point. A little nitrobenzene has the same effect.

2. *With Pure Iodine*

Commercial iodine is contaminated with chlorine, bromine, water, and sometimes cyanogen; it must be purified. For this purpose grind 5 or 6 g of the commercial product with 2 g of potassium iodide; any chlorine or bromine present forms potassium chloride or bromide, setting free an equivalent amount of iodine. Place the mixture in a dry casserole (Fig. 14)[1] which rests in a muffle. Upon the casserole place a flask filled with cold water. Have a wire gauze at the bottom of the muffle and a Bunsen flame beneath this. The iodine sublimes rapidly and collects as a crystalline crust on the bottom of the flask, and practically none of it is lost. As soon as the evolution of violet vapors from the bottom of the casserole has practically ceased, the sublimation is complete. Remove the flame and, after allowing to cool, take away the flask with the iodine adhering to it. To remove the iodine, pass a current of cold water through the

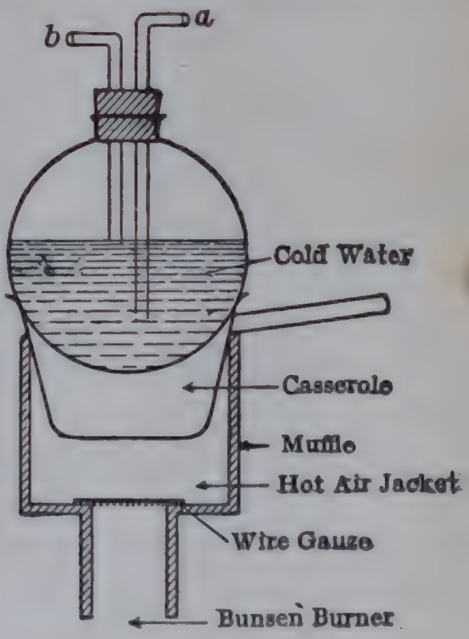

FIG. 14.

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[1] C. R. McCrosky, *J. Am. Chem. Soc.*, **40**, 1664 (1918).

tube *a* into the flask and out at *b*. This causes the glass to contract somewhat and the whole of the iodine crust can be removed by lightly scraping with a clean glass rod. Catch it upon a watch glass, break it up into large pieces, and repeat the sublimation without the addition of potassium iodide at as low a temperature as possible; in this way a product free from potassium iodide is obtained. Grind the iodine somewhat in an agate mortar and dry in a desiccator containing calcium chloride. If dried over sulfuric acid, some of the acid is likely to be present in the iodine. Furthermore, the cover of the desiccator must not be greased, for grease is attacked by iodine vapors, forming hydriodic acid, which might cause contamination.

Weighing out the Iodine. In each of 2 or 3 small weighing tubes with tightly fitting glass stoppers place 2–2.5 g of pure potassium iodide free from iodate and 0.5 ml of water (not more); stopper the tubes and weigh accurately. Then open the tubes and add 0.4–0.5 g of pure iodine to each. Quickly insert the stopper and again weigh; the difference shows the amount of iodine. As the tubes are cooled by the dissolving of the iodine, moisture sometimes collects on the outside and must be wiped off before weighing. The iodine dissolves almost instantly in the concentrated potassium iodide solution. Place one of the tubes in the neck of a 500-ml Erlenmeyer flask which is held in an inclined position and contains 200 ml of water and about 1 g of potassium iodide. Drop the tube to the bottom of the flask, but just as it begins to fall remove the stopper and allow it to follow. In this way no iodine is lost, which is likely to happen if the contents of a tube are washed into the water. A solution is thus prepared containing a known amount of iodine. To it add the sodium thiosulfate solution to be standardized from a buret until the liquid is pale yellow. Then add 2 or 3 ml of starch solution and carefully titrate until colorless. From the mean of two or three determinations, the strength of the thiosulfate solution is calculated.

If the weight of iodine equivalent to 1 ml of sodium thiosulfate solution is divided by 0.1269 (the milliequivalent of iodine), the *normality* of the solution will be obtained.

3. *With Potassium Permanganate* (*Volhard*)

On adding potassium permanganate to an acid solution containing potassium iodide, the following reaction takes place:

$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{++} + 8H_2O + 5I_2$$

The reaction is quantitative if the correct conditions are maintained.

Measure out 25–40 ml of standardized tenth-normal permanganate solution from a pipet or buret into a 300-ml Erlenmeyer flask containing 3 g of potassium iodide, 50 ml of water, and 5 ml of concentrated hydrochloric acid. Let stand in the dark for 3 minutes, dilute to 200 ml, and titrate slowly with the thiosulfate solution, adding 2 ml of starch indicator solution toward the last.

4. *With Potassium Dichromate*

The reaction between potassium dichromate and potassium iodide can also be used for the standardization of sodium thiosulfate solutions; the dichromate is reduced to green chromic salt, an equivalent weight of iodine being set free provided the solution is 0.2–0.4 N in acid.

$$Cr_2O_7^{--} + 6I^- + 14H^+ \rightarrow 2Cr^{+++} + 3I_2 + 7H_2O$$

Prepare tenth-normal potassium dichromate solution by dissolving 4.903 g of the pure, dry salt in water and diluting to 1 l at 20° in a measuring flask. Mix well by pouring back and forth from the flask to a beaker at least 4 times. Measure out 20–40 ml of the dichromate solution, with a pipet or buret, into a 500-ml beaker containing 50 ml of water, 10 ml of concentrated hydrochloric acid, and 3 g of potassium iodide. Allow the reaction to proceed in the dark for 5 minutes, then dilute to 400 ml and titrate with tenth-normal thiosulfate solution, adding starch toward the last.

Preparation of Tenth-Normal Iodine Solution

No advantage is obtained by dissolving the desired quantity of sublimed iodine in a definite volume of solution, for the latter cannot be kept very long unchanged. It is more practical to prepare the iodine solution by placing 20–25 g of pure potassium iodide in a liter bottle, dissolving it in as little water as possible, and then adding about 12.7 g of commercial iodine, weighed out roughly on a watch glass. Shake the contents of the flask until all the iodine is dissolved. When this is accomplished, dilute the solution to about 1 l and standardize according to one of the following methods. The solution should be used in a glass-stoppered buret.

Standardization of Iodine Solution

1. *With 0.1 N Sodium Thiosulfate Solution*

Take 25 ml of the well-mixed iodine solution in a 250-ml Erlenmeyer flask, dilute to 100 ml and introduce 0.1 N $Na_2S_2O_3$ solution until nearly all the iodine has reacted as shown by the color. Add 1 ml of starch paste and titrate slowly until colorless.

Remark. To titrate a solution of iodine obtained from a solution of iodide-iodate mixture, titrate in the same way but in the presence of 20 millimoles of free hydrochloric acid.

2. *With Arsenious Acid*

If iodine is allowed to act upon a neutral solution of arsenious acid the reaction which takes place may be expressed as follows:

$$H_2AsO_3^- + I_2 + 2HCO_3^- = H_2AsO_4^- + 2I^- + H_2O + 2CO_2$$

It is necessary to keep the solution neutral or the opposite reaction will take place.

$$H_2AsO_4^- + 2I^- + 6H^+ = As^{+++} + I_2 + 4H_2O$$

In a neutral solution arsenite can be oxidized quantitatively by means of free iodine, but in strongly acid solution arsenic acid can be reduced quantitatively to the trivalent condition by means of iodide. To accomplish a complete oxidation of the arsenic by iodine, it is necessary to keep the solution approximately neutral to phenolphthalein. This is usually accomplished by providing an excess of sodium bicarbonate, by adding normal sodium carbonate to the cold acid solution, or by adding some disodium phosphate. Caustic alkali cannot be used because it reacts with iodine to form hypoiodite and iodide. A little neutral sodium carbonate does no harm if added to an acid solution because the liberated carbon dioxide neutralizes the hydroxyl ion formed by hydrolysis of the carbonate.

From the above equation, and the fact that the valence change of arsenic is 2, it follows that the equivalent weight of arsenic is one-half the atomic weight. Ordinarily, the arsenite solution is prepared by weighing out pure As_2O_3. As the molecule contains 2 atoms of arsenic, it is evident that one-fourth the molecular weight in grams is the equivalent weight of As_2O_3.

To prepare 0.1 *N* arsenious acid solution, dissolve 4.946 g of the pure sublimed oxide and 15 g of sodium carbonate by warming with 150 ml of water. Transfer the solution to a liter measuring flask, add 25 ml of normal acid, and dilute at 20° to the mark.

To prepare pure arsenious oxide from the commercial product, sublime by heating in a porcelain dish and collect the sublimate on a watch glass. If a yellow sublimate of sulfide is noticed, dissolve the sample in hot 4 *N* hydrochloric acid, filter off the undissolved sulfide, and cool the filtrate to cause crystals to deposit. Filter, wash with water, and then sublime. Dry over calcium chloride in a desiccator.

Titrate the arsenite against the iodine solution in the usual way. Deiss,[1] however, finds that iodine gradually changes to iodate on standing and the iodate does not react with arsenic in the presence of sodium bicarbonate. He proceeds as follows:

Add 25 ml of the iodine solution to 200 ml of water. Add 2 ml of 6 N hydrochloric acid and then 2 g of sodium bicarbonate. As soon as it has dissolved titrate with sodium arsenite.

A solution of sodium arsenite gradually oxidizes on long standing.[2]

ANALYSES BY IODIMETRIC METHODS

1. Determination of Copper

1 l of 0.1 N $Na_2S_2O_3$ solution = Cu/10 = 6.357 g Cu ✓

Principle. If a solution of a cupric salt at a suitable concentration is treated with an excess of potassium iodide, all the copper is precipitated as cuprous iodide, and there is liberated one atom of iodine for each atom of copper present, $2Cu^{++} + 4I^- \rightarrow Cu_2I_2 + I_2$. The iodine is titrated with sodium thiosulfate solution. The method was studied by Gooch and Heath,[3] who found that the quantity of potassium iodide used, the concentration of the solution, and the quantity of acid present are three factors which must be taken into consideration. In a volume of 50 ml an excess of 0.6–1.0 g of potassium iodide is sufficient to cause the complete precipitation of 0.0020 g of copper, but in a volume of 100 ml an excess of 3–5 g is desirable. In general, the more dilute the solution, the greater the quantity of potassium iodide required. A larger excess of potassium iodide does no harm.

A little free acid does no harm, but not more than 2 ml of concentrated mineral acid may be present in 50 ml of solution.

If an appreciable amount of arsenic is present, mineral acids must not be present on account of their tendency to bring about the reduction of the higher salts of arsenic and antimony when an excess of potassium iodide is used. Obviously the solution must not contain any other oxidizing agent.

Two procedures will be given for the determination of copper in an ore. In the first method, the sample is dissolved in nitric acid, or aqua regia, and the solution is evaporated with sulfuric acid to form insoluble lead sulfate if lead is present. The insoluble residue together with lead sulfate is filtered off and the solution boiled with aluminum which precipitates copper and reduces ferric iron. The copper is filtered off and dissolved in nitric acid; after this the procedure is practically the same as in the standardization against copper wire. The purpose of precipitating the copper with aluminum is to separate it from iron which, in the ferric condition, is reduced by potassium iodide.

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[1] *Chem. Ztg.* **38**, 413.

[2] S. W. Young, *J. Am. Chem. Soc.*, **26**, 1028 (1904).

[3] F. A. Gooch and F. H. Heath, *Am. J. Sci.*, [4], **24**, 68 (1907); F. H. Heath, *ibid.*, [4], **25**, 513 (1908).

This method is accurate but long. Low himself recommended a shorter procedure for ordinary work. In the short method recommended by him, the solution was evaporated to dryness and the dry residue was leached with strong ammonia solution which dissolved out the cupric salt as blue cupric ammonia complex and left the iron behind. After the solution was made acid with acetic acid, it was treated with potassium iodide and the liberated iodine titrated with thiosulfate. After some practice with this short method good results can be obtained, but if the residue has become baked, often some of the copper does not dissolve, whereas if the evaporation has taken place during constant rotation of the flask while being heated over a free flame and the heating is stopped as soon as the residue is dry, the extraction of all the copper is possible if sufficient salt, such as potassium chloride, is present.

It has been found, however, that it is possible to avoid the separation of the copper from the iron if some substance, such as fluoride, is added to convert the ferric cations into a slightly ionized complex. Then, if the solution is buffered to give the proper hydrogen-ion concentration, the solution can be titrated just as if no iron were present. The method of Bartholow Park,[1] which will be described after that of Haën-Low, is based upon this principle.

(a) *Method of Haën[2]-Low[3]*

Procedure. To 0.25–0.50 g of fine ore weighed into a 250-ml Erlenmeyer flask, add 6 ml of 16 *N* HNO_3, and boil gently until nearly dry. Add 5 ml of 12 *N* HCl and heat again. As soon as the incrusted matter has dissolved add 12 ml of 18 *N* H_2SO_4 and heat until the acid fumes freely. Cool and add 25 ml of water. Then heat until any anhydrous ferric sulfate is dissolved, and filter to remove insoluble sulfates and silica. Wash the flask and filter paper with hot water until the volume of the filtrate amounts to about 75 ml, receiving it in a 150-ml beaker. Take a strip of aluminum about 2.5 cm wide and 14 cm long, bend it into a triangle, and place it in the beaker resting on its edge. Cover the beaker and boil gently for 7–10 minutes, which will be sufficient to precipitate all the copper, provided that the solution does not much exceed 75 ml. Avoid boiling to a very small volume. The aluminum should now appear clean, the copper being detached or loosely adhering. Remove from the heat, and wash down the cover and sides of the beaker with hydrogen sulfide water. This will prevent oxidation and will also serve to precipitate the last traces of copper. If the hydrogen sulfide shows that more than a very little copper remained in solution, it is best to dilute the solution to 75 ml again and to boil a little longer. This will coagulate the sulfide. Finally, decant through a filter and then, without delay, transfer the precipitate to the filter with the aid of a stream of hydrogen sulfide water from a wash bottle. Let the strip of aluminum remain in the beaker, but wash it as clean as possible with the hydrogen sulfide water. Wash the filter and precipitate at least 6 times with this hydrogen sulfide water, but take care not to let the filter remain empty for any length of time. Moist copper sulfide oxidizes very rapidly when in contact with the air with the formation of a little copper sulfate, which will dissolve and pass through the filter only to precipitate again when it comes in contact with the filtrate containing hydrogen sulfide.

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[1] *Ind. Eng. Chem., Anal. Ed.*, **3**, 77 (1931).

[2] *Ann. Chem. Pharm.*, **91**, 237 (1854).

[3] *Technical Methods of Ore Analysis.*

Now place the original clean flask under the funnel, perforate the filter, and rinse the precipitate into the flask with hot water, using as little as possible. Lift the fold of the filter and rinse down any precipitate found beneath the fold. Using a small pipet, allow 5 ml of strong nitric acid to run over the aluminum in the beaker and pour it from the beaker through the filter into the flask, but do not wash the beaker or filter at this stage. Remove the flask and replace it with the beaker. Heat the contents of the flask to dissolve the copper and expel the red fumes, then again place the flask under the funnel. Now pour over the filter 5 ml or more of bromine water, using enough to impart a strong color to the solution in the flask. Next wash the beaker and aluminum, pouring the washings through the filter. Finally wash the filter 6 times with hot water. Boil till the solution is reduced to about 25 ml, cool somewhat, and add a slight excess of strong ammonia (about 7 ml). Boil off the excess of ammonia, add an excess of acetic acid, and boil a minute longer. Cool to room temperature, add 3 g of potassium iodide, and titrate with sodium thiosulfate solution, adding starch toward the last.

(*b*) *Method of Park*

Dissolve the sample exactly as described in the above method of Haën-Low and continue exactly as described there but receive the filtrate obtained after heating to fumes of H_2SO_4, diluting and filtering off the unsoluble residue, in a 250-ml Erlenmeyer flask. Concentrate to about 30 ml, cool, and add ammonium hydroxide until a slight permanent precipitate (usually $Fe(OH)_3$) is formed or the solution begins to turn a permanent blue. Heat if necessary to remove excess ammonia. Add 2 g of ammonium bifluoride, weighed to the nearest centigram, and 1 g of potassium acid phthalate, also weighed to the nearest centigram. When the solution is clear, add approximately 3 g of potassium iodide and titrate at once with thiosulfate solution, adding starch toward the last.

With the above conditions the pH of the solution is about 4 and antimony or arsenic is not reduced by the iodide. Ferric iron is not reduced because it is present for the most part as FeF_6^{---} anions.

2. Determination of Antimony in Stibnite

1 ml of normal iodine solution = 0.06088 g Sb

Principle. Stibnite, Sb_2S_3, dissolves in 12 *N* normal hydrochloric acid with evolution of hydrogen sulfide.

$$Sb_2S_3 + 8HCl \rightarrow 2HSbCl_4 + 3H_2S \uparrow$$

After the hydrogen sulfide has been removed, tartaric acid is added to form the antimonyl tartrate ion, which is so stable that it prevents the hydrolysis of the antimony salt upon dilution:

$$SbCl_4^- + H_2C_4H_4O_6 + H_2O \rightarrow H(SbO)C_4H_4O_6 + 3H^+ + 4Cl^-$$

The final titration takes place as follows:

$$H(SbO)C_4H_4O_6 + I_2 + 2HCO_3^- \rightarrow H(SbO_2)C_4H_4O_6 + 2I^- + H_2O + 2CO_2 \uparrow$$

Weigh out 0.2–0.3 g of stibnite into a 150-ml beaker, cover with a watch glass, and add 10 ml of concentrated hydrochloric acid. Allow the acid to act in the cold for 10 minutes, add 0.3 g of solid potassium chloride, and heat gently on the water bath for 15 minutes to complete the attack and expel hydrogen sulfide. Take care not to allow the liquid to evaporate sufficiently to expose any part of the bottom of the beaker. There is usually a silicious residue, insoluble in hydrochloric acid.

Remove the beaker from the water bath, cool to room temperature, and add a solution of 3 g of tartaric acid which has been dissolved by heating in a test tube with 5 ml of water and cooled under running water. Mix well by rotating the contents of the beaker. Slowly add water, while stirring, to a volume of about 100 ml.

Pour this solution slowly, while stirring, into a 600-ml beaker containing 10 g of sodium carbonate dissolved in 200 ml of cold water. This serves to neutralize the acid and provide sufficient sodium bicarbonate to keep the solution neutral during the iodine titration. Wash down the sides of the beaker, add starch paste, and titrate with iodine to the appearance of a permanent blue.

If a fugitive end point is obtained, SbOCl has been precipitated or not enough sodium bicarbonate is present.

Remarks. Antimony chloride is volatile with steam from its concentrated, hydrochloric acid solutions, but the heating on the water bath can be carried out, without fear of losing antimony, if the acid is not allowed to evaporate too much and KCl is present to form less volatile $KSbCl_4$. This heating serves to remove all the hydrogen sulfide which would otherwise precipitate the antimony as trisulfide upon diluting the solution. If insufficient tartaric acid is present, antimony oxychloride, SbOCl, precipitates; and if the solution is titrated in this condition it is impossible to obtain a permanent end point.

3. Determination of Iron

1 l of 0.1 N $Na_2S_2O_3$ solution = Fe/10 = 5.584 g Fe

This method, first proposed by Carl Mohr,[1] is based upon the following reaction:

$$2FeCl_3 + 2HI \rightleftarrows 2HCl + 2FeCl_2 + I_2$$

As the reaction is reversible, it is necessary to have an excess of hydriodic acid present in order that it may take place quantitatively in the direction from left to right.

When carried out in the presence of air, a very little of the hydriodic acid is probably oxidized by the air, but in the following procedure this error is counterbalanced almost exactly by the fact that the reduction of the iron is not quite complete. If sulfuric acid is present, higher concentrations of both acid and iodide are required and the end point is less stable.

Procedure. To about 30 ml of ferric chloride solution in a 200-ml Erlenmeyer flask containing 0.1–0.15 g of iron and 0.25–25 milliequivalents of hydrochloric acid, add 3 g of solid potassium iodide, stopper the flask, and allow to stand for 5 minutes. Dilute to about 100 ml and titrate with 0.1 N thiosulfate solution, adding starch solution toward the last.

4. Determination of Hydrogen Sulfide

1 l of 0.1 N $Na_2S_2O_3$ solution = $H_2S/20$ = 1.704 g H_2S

If an acid solution of hydrogen sulfide is treated with iodine, the sulfide is oxidized with separation of sulfur: $H_2S + I_2 = 2HI + S$. The solution must not react basic as then some sulfide will be oxidized to sulfate and some iodine will react with OH to form iodide and iodate ions.

For the determination of the amount of the gas present in hydrogen sulfide water, transfer a measured amount by means of a pipet to a known volume of 0.1 N iodine solution and titrate the excess of the latter with thiosulfate solution.[2]

If the amount of hydrogen sulfide present is not very large, correct results are obtained without difficulty. With considerable hydrogen sulfide, on the other hand, the deposited sulfur is likely to enclose some of the iodine solution, as shown by its brown color; this iodine escapes the titration with thiosulfate. In such a case, remove the film of sulfur floating on the surface of the liquid with a glass rod after the completion of the thiosulfate titration, transfer it to a glass-stoppered cylinder, and shake with 1–2 ml of carbon bisulfide. This dissolves the iodine with a violet color, and the color can be discharged with sodium thisulfate solution.[1] In this way the total amount of the iodine that remains can be titrated.

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[1] *Ann. Chem. Pharm.*, **105**, 53. Cf. Kolthoff, *Pharm. Weekblad*, 58, 1510 (1921); Böttger and Böttger, *Z. anal. Chem.*, **70**, 214; Grey, *J. Chem. Soc.*, **1929**, 35; Swift, *J. Am. Chem. Soc.*, **51**, 2682 (1929).

[2] Correct results cannot be obtained by titrating directly with iodine; cf. O. Brunck, *Z. anal. Chem.*, **45**, 541 (1906).

Remark. This method can be used to advantage for determining the sulfur present in soluble sulfides.

5. Analysis of Sulfide and Hydrosulfide Mixtures

$$1 \text{ l of } 0.1\ N \text{ iodine solution} = \begin{cases} 1.704 \text{ g } H_2S \\ 2.803 \text{ g } NaHS \\ 3.903 \text{ g } Na_2S \end{cases}$$

Principle. If a solution of alkali sulfide and alkali hydrosulfide is treated with an acid solution of iodine, the following reactions take place:

$$(a)\quad Na_2S + 2HCl = 2NaCl + H_2S$$
$$(b)\quad NaSH + HCl = NaCl + H_2S$$
$$(c)\quad H_2S + I_2 = 2HI + S$$

Hydrogen sulfide is a very weak acid, without effect upon phenolphthalein indicator. After oxidation, the hydrogen sulfide is replaced by the strong mineral acid, hydriodic acid.

It is evident from the above equations that in the case of the sulfide, the quantity of hydriodic acid formed by the oxidation of the hydrogen sulfide is equivalent to the quantity of hydrochloric acid required to decompose the sulfide. In the case of the hydrosulfide, however, which is the acid salt of hydrogen sulfide, the quantity of hydriodic acid formed is equivalent to twice the quantity of hydrochloric acid required to decompose the hydrosulfide.

By determining the quantity of acid or base present at the start, the acidity at the end of the analysis, and the quantity of iodine used in oxidizing the sulfide to free sulfur, one can distinguish between the following possibilities, in which it is assumed that any strong acid present is hydrochloric acid and any base is sodium hydroxide. The reasoning applies, of course, to cases where other strong acids or other bases are present. The solution may contain:

(1) Sodium hydroxide, NaOH, and sodium sulfide, Na_2S.
(2) Sodium sulfide alone.
(3) Sodium sulfide, Na_2S, and sodium hydrosulfide, NaHS.
(4) Sodium hydrosulfide alone.

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[1] The separation of the sulfur into a coherent film can be prevented by sufficiently diluting the solution with boiled water. O. Brunck (*Z. anal. Chem.*, **45**, 541) therefore, recommends using 0.01 *N* iodine instead of 0.1 *N* solution, and this is certainly advisable with small quantities of hydrogen sulfide as, for example, in a mineral water. On the other hand, when a relatively large volume of hydrogen sulfide is liberated from a sulfide by means of acid it is advisable to use 0.1 *N* iodine, as otherwise the volume of solution will be too large unless a very small weight of substance is used in the analysis.

(5) Sodium hydrosulfide, NaHS, and hydrogen sulfide, H_2S.
(6) Hydrogen sulfide alone.
(7) Hydrogen sulfide, H_2S, and hydrochloric acid, HCl.

Any other possibility is excluded because sodium hydroxide and sodium hydrosulfide react to form sodium sulfide; sodium sulfide and hydrogen sulfide react to form sodium hydrosulfide; sodium hydrosulfide and hydrochloric acid react to form hydrogen sulfide. We may regard these last three reactions as taking place practically completely because there is a great difference in the ionization constants of HCl, H_2S and HS^-.

Now let us consider what will happen in the analysis of the seven mixtures just mentioned. In the analysis let us assume that a milliequivalents of iodine solution together with b milliequivalents of hydrochloric acid are added at the start. The excess iodine is titrated with c milliequivalents of sodium thiosulfate, and after that d milliequivalents of sodium hydroxide are added to make the solution neutral to phenolphthalein. From these four values, a, b, c, and d, we can easily compute the quantity of NaOH, Na_2S, NaHS, H_2S, and HCl originally present, but, as just explained, the only possible combinations will be two neighboring compounds, NaOH and Na_2S, Na_2S and NaHS, NaHS and H_2S, H_2S and HCl.

(1) In this case, the hydrochloric acid added at the beginning of the analysis will be neutralized by both NaOH and Na_2S. The quantity of iodine required will be equivalent to the sulfide present, and, since the weak hydrogen sulfide becomes strong hydriodic acid, just as much hydriodic acid will be formed as was required of hydrochloric acid to liberate hydrogen sulfide from the sodium sulfide.

$$a - c = \text{milliequivalents of sulfide present}$$

$$b - d = \text{milliequivalents of NaOH}$$

The molecular weight of Na_2S divided by 2000 is the milliequivalent weight of Na_2S.

(2) In the second case, when sodium sulfide alone is present, $b = d$ and $a - c =$ milliequivalents of sulfide as in case (1).

(3) When sodium sulfide and sodium hydrosulfide are both present, the relations are a little more complicated. As in the previous cases, $a - c =$ the milliequivalents of sulfide present, and the milliequivalents of sodium sulfide and of sodium hydrosulfide from the standpoint of iodimetry are the molecular weight divided by 2000 in each case. The value d in this case is greater than b; $d - b =$ the milliequivalents of NaHS present and $a - c > 2(d - b)$ because the milliequivalent weight of sodium hydrosulfide from the acidimetric standpoint is one-thousandth of the molecular weight. Therefore, if we subtract from $a - c$ (the total milliequivalents of iodine required for Na_2S and NaHS) twice the value of $d - b$, the difference will be the milliequivalents of Na_2S present.

(4) Here $a - c = 2(d - b)$. The NaHS content can be computed from either $a - c$ or from $d - b$, but we must remember to divide the molecular weight of NaHS by 2000 if we wish to find the milliequivalent from the iodimetric standpoint and by 1000 if we wish to find the milliequivalent from the acidimetric standpoint.

(5) When NaHS and H_2S are present, $a - c < 2(d - b)$. Here, as in every other case, the milliequivalent of each sulfide is the molecular weight divided by 2000 from the iodimetric standpoint. With respect to the HI formed by the action of iodine, the milliequivalent weight of NaHS is the molecular weight divided by 1000, but with hydrogen sulfide it is the molecular weight divided by 2000 exactly as

in the iodine titration. If we call n_1 the number of millimoles of NaHS and n_2 the millimoles of H_2S, then

$$2n_1 + 2n_2 = a - c$$

$$n_1 + 2n_2 = d - b$$

(6) When hydrogen sulfide alone is present

$$a - c = d - b$$

(7) When hydrogen sulfide and hydrochloric acid are present, $a - c < d - b$. From the value of $a - c$ the quantity of H_2S can be computed, and by subtracting $a - c$ from $d - b$ the milliequivalents of HCl present are found.

In any case, therefore, all we have to do is to compare the milliequivalents of iodine with the milliequivalents of acid or base required to neutralize the solution after the iodine titration. Calling the former value T_1 ($a - c$ in the above notation) and the latter value T_2 ($d - b$ in the above notation), the above seven cases can be summarized as follows:

(1) In determining T_2, we find that $b > d$. The solution contains NaOH and Na_2S.
(2) $T_2 = 0$. Na_2S alone is present.
(3) $T_1 > 2T_2$. Na_2S and NaHS are present.
(4) $T_1 = 2T_2$. NaHS alone is present.
(5) $T_1 < 2T_2$. NaHS and H_2S are present.
(6) $T_1 = T_2$. H_2S alone is present.
(7) $T_1 < T_2$. H_2S and HCl are present.

The student naturally inquires at this point whether such a study is of great importance. No such claim can be made. There is really no need for asking the student to carry out such an analysis in the laboratory in an elementary course of instruction. On the other hand, it is profitable for him to try to understand these relations, for such problems do actually arise in chemical practice and, if he understands what is meant by an equivalent weight, there is no reason why he should find great difficulty in following the above reasoning. Confusion arises from the fact that the milliequivalent weight varies in accordance with the nature of the chemical reaction involved. The mathematical computations involve nothing more difficult than elementary algebra.

Procedure. Dilute a known volume of 0.1 *N* iodine together with a known volume of 0.1 *N* hydrochloric acid[1] in a beaker to a volume of about 400 ml, and slowly add the solution containing the dissolved sulfide from a buret with constant stirring, until the mixture becomes pale yellow. Add starch indicator and titrate the excess of iodine with tenth-normal thiosulfate solution. Finally, titrate the acid in the solution with 0.1 *N* sodium hydroxide solution, using phenolphthalein as indicator. Calculate the results as outlined above.

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[1] Enough acid to decompose all sulfide must be present. An excess does no harm.

6. Determination of Copper with Potassium Iodate[1]

Potassium iodate in dilute hydrochloric acid solution is reduced by potassium iodide to free iodine:

$$KIO_3 + 5KI + 6HCl = 6KCl + 3I_2 + 3H_2O$$

but if the solution is strongly acid with hydrochloric acid and an excess of the iodate is added, the iodine is oxidized to ICl:

$$2I_2 + KIO_3 + 6HCl = KCl + 5ICl + 3H_2O$$

and in this case the whole reaction may be expressed by the equation:

$$KIO_3 + 2KI + 6HCl = 3KCl + 3ICl + 3H_2O$$

The ICl is not very stable, and is at once reduced to free iodine in the presence of any oxidizable substance.

L. W. Andrews[2] has shown that quite a number of substances capable of reducing iodate, such as free iodine, iodides, arsenites, and antimonites, can be titrated with potassium iodate very exactly, by taking advantage of the fact that, when the reducing agent is present in excess, free iodine is formed which is oxidized quantitatively by more iodate, provided that the proper amount of hydrochloric acid is present. Copper solutions are precipitated quantitatively by potassium thiocyanate and sulfurous acid as cuprous thiocyanate, CuSCN, and Parr[3] has estimated copper quantitatively by titrating this precipitate with permanganate. The oxidation is simpler and more accurate, however, when the titration is effected by potassium iodate or biiodate. The reaction goes through the stage in which iodine is set free, but the iodine is oxidized completely to iodine chloride upon the addition of more iodate:

(*a*) $10CuSCN + 14KIO_3 + 14HCl = 10CuSO_4 + 7I_2 + 10HCN + 14KCl + 2H_2O$

(*b*) $2I_2 + KIO_3 + 6HCl = KCl + 5ICl + 3H_2O$

and the whole reaction is

(*c*) $4CuSCN + 7KIO_3 + 14HCl = 4CuSO_4 + 7ICl + 4HCN + 7KCl + 5H_2O$

The potassium iodate solution is very stable and can be preserved for years if protected from evaporation. The standard solution used can be prepared by weighing out a known amount of the pure salt and dissolving to a definite volume, or the solution can be standardized against pure copper, carrying out the process as in an analysis. A convenient concentration is ⅕ mole KIO_3 per liter.

Procedure. To 0.5 g of the ore in a 200-ml flask, add 6–10 ml of strong nitric acid, and boil gently, preferably over a free flame, keeping the flask in constant motion and inclined at an angle of about 45°, until the larger part of the acid has been removed. If this does not completely decompose the ore, add 5 ml of strong hydrochloric acid and continue the boiling until the volume of liquid is about 2 ml. Now add gradually and carefully, after cooling somewhat, 12 ml of 18 *N* sulfuric acid, and continue the boiling until sulfuric acid fumes are evolved copiously. Allow to cool, add 25 ml of cold water, heat to boiling, and keep hot until the soluble sulfates have dissolved. Filter into a beaker, and wash the flask and filter thoroughly with cold water.[1] Nearly neutralize the filtrate with ammonia and add 10–15 ml of strong sulfur dioxide water. Heat just to boiling and add 5–10 ml of a 10 per cent solution of ammonium thiocyanate, according to the amount of copper present. Stir thoroughly, allow the precipitate to settle for 5 to 10 minutes, filter on paper, and wash with hot water until the excess ammonium thiocyanate is removed completely.

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[1] Jamieson, Levy, and Wells, *J. Am. Chem. Soc.*, **30**, 760 (1908).

[2] *Ibid.*, **25**, 756 (1903).

[3] *Ibid.*, **22**, 685 (1900).

Place the filter with its contents in a glass-stoppered bottle of about 250-ml capacity, and by means of a piece of moist filter paper transfer into the bottle any precipitate adhering to the stirring rod and beaker. Add to the bottle about 5 ml of chloroform, 20 ml of water, and 30 ml of concentrated hydrochloric acid (the two last liquids may have been mixed previously). Now run in standard potassium iodate solution, inserting the stopper and shaking vigorously between additions. A violet color appears in the chloroform, at first increasing and then diminishing, until it disappears with great sharpness. The rapidity with which the iodate solution may be added can be judged from the color changes of the chloroform.

To make another titration it is not necessary to wash the bottle or throw away the chloroform. Pour off two-thirds or three-fourths of the liquid in order to remove most of the pulped paper, too much of which interferes with the settling of the chloroform globules after agitation, add enough properly diluted acid to make about 50 ml, and proceed as before. In this case, where iodine monochloride is present at the outset, the chloroform becomes strongly colored with iodine as soon as the cuprous thiocyanate is added, but this makes no difference in the results of the titration.

7. Iodimetric Analysis of Chromite

Principle. The chromium of chromite, $FeCr_2O_4$, is oxidized to Na_2CrO_4 by fusion with sodium peroxide. The melt is leached with water, and the insoluble residue is dissolved in hydrochloric acid, added in slight excess. Ammonium fluoride is then added to convert Fe^{+++} into FeF_6^{---}; the former ions are reduced by hydriodic acid but the latter are unaffected. Then to the acid solution an excess of potassium iodide is added and the liberated iodine is titrated with sodium thiosulfate solution in the presence of starch as indicator.

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[1] With substances containing appreciable amounts of silver a few drops of hydrochloric acid should be added before making this filtration, but not enough to dissolve any considerable amounts of the lead sulfate or antimonic oxide that may be present.

$$2FeCr_2O_4 + 7Na_2O_2 \rightarrow 2NaFeO_2 + 4Na_2CrO_4 + 2Na_2O \text{ (fusion)}$$

$$\left.\begin{array}{l} NaFeO_2 + 2H_2O \rightarrow Na^+ + \mathbf{Fe(OH)_3} + OH^- \\ 2Na_2O_2 + 2H_2O \rightarrow 4Na^+ + 4OH^- + O_2 \end{array}\right\} \text{ (water added)}$$

$$\left.\begin{array}{l} 2CrO_4^{--} + 2H^+ \rightarrow Cr_2O_7^{--} + H_2O \\ \mathbf{Fe(OH)_3} + 3H^+ \rightarrow Fe^{+++} + 3H_2O \end{array}\right\} \text{ (acid added)}$$

$$Fe^{+++} + 6F^- \rightarrow FeF_6^{---} \text{ (fluoride added)}$$

$$Cr_2O_7^{--} + 6I^- + 14H^+ \rightarrow 2Cr^{+++} + 3I_2 + 7H_2O \text{ (iodide added)}$$

$$I_2 + 2S_2O_3^{--} \rightarrow 2I^- + S_4O_6^{--} \text{ (titration)}$$

From these equations, it is evident that the milliequivalent weight of chromium is the atomic weight divided by 3000 as in the analysis with potassium dichromate (p. 105).

For the fusion, an iron crucible of about 25-ml capacity is commonly used. A nickel crucible is attacked less by the peroxide fusion, and the presence of nickel has been found advantageous for the decomposition of the excess peroxide, but it is usually necessary to filter the solution after making it acid when a nickel crucible is used, and the nickel crucible costs considerably more. A porcelain crucible has also been recommended, but this again is more expensive than the iron. The fusion can also be carried out in a test tube.

Procedure. Weigh out 0.3–0.4 g of chromite and fuse with sodium peroxide exactly as described on p. 105. Continue as directed there down to the point where the solution is made acid. Then, instead of sulfuric acid, add hydrochloric acid until all the hydrated ferric oxide has dissolved. Use 1 ml of concentrated hydrochloric acid in excess for each 100 ml of solution. Add 2 g of ammonium fluoride, more if necessary, until a small drop of the solution will give no test for Fe^{+++} with potassium ferrocyanide solution on the spot plate. Add 3 g of potassium iodide, wait 3 minutes, and then titrate with sodium thiosulfate solution. Add starch solution toward the last.

HOME PROBLEMS

70. What weight of stibnite should be taken for analysis so that the number of milliliters of 0.08 *N* iodine used to oxidize the antimony from the trivalent to quinquevalent condition is the same number as the percentage of antimony present? What weight should be taken for the same analysis so that the buret reading gives the percentage of Sb_2S_3 directly?

71. If a copper ore containing 23.4 per cent of copper is analyzed by Low's iodimetric method, how many milliliters of thiosulfate will be used for a sample weighing 0.5 g? Thirty milliliters of the thiosulfate reacts with iodine liberated from potassium iodide and 25 ml of $KMnO_4$, of which 1 ml = 0.00705 g of $Na_2C_2O_4$.

72. If the same weight of the same copper ore were analyzed by the method of Jamieson, Levy, and Wells, how many milliliters of KIO_3 solution containing $\frac{1}{20}$ mole per liter would be used?

73. A solution contains soluble sulfide. On the assumption that nothing else is present that reacts with iodine or that is acidic or basic, and that the sulfide

is either H_2S, NaSH, or Na_2S, compute the weight of H_2S, NaSH, or Na_2S present in 100 ml of solution. (Assume that Na_2S and H_2S cannot both be present as a mixture of these two reacts to form NaSH.)

One hundred fifty milliliters of solution was poured into a mixture of 30 ml of 0.25 *N* HCl, 50 ml of 0.120 *N* I_2 solution, and 320 ml of water. The excess I_2 reacted with 8 ml of 0.125 *N* $Na_2S_2O_3$. Then it required 30 ml of 0.3 *N* NaOH to neutralize the solution.

74. Same problem except that the final volume of NaOH used was 40 ml.

75. Compute the percentage of chromium in a mineral from the following data: weight of sample = 0.38 g; added 2.58 g of NH_4F, 3.25 g of KI, and 46.20 ml of $Na_2S_2O_3$ of which 1 ml = 0.0054 g Cu.

76. What weight of chromite should be taken for analysis by the iodimetric method so that 2 ml of 0.108 *N* $Na_2S_2O_3$ solution will correspond to 1.5 per cent of chromium in the sample?

77. The lead in 0.5670 g of an ore is deposited electrolytically as PbO_2. The deposit is dissolved in an acid solution of KI, and the liberated iodine is titrated with 36.23 ml of 0.0998 *N* thiosulfate. Calculate the percentage of lead in the ore.

78. From 0.567 g of an ore, the lead was precipitated as $PbCrO_4$, the precipitate was dissolved in an acid solution of KI, and the liberated iodine was titrated with 54.34 ml of 0.0998 *N* thiosulfate. Calculate the percentage of Pb in the ore.

79. A sample of bleaching powder contains 50 per cent "available" chlorine. How many grams of 3 per cent hydrogen peroxide will be required to reduce all the hypochlorite in 2.0 g of the sample, and what volume of oxygen measured dry at 25° and 760 ml pressure will be evolved according to the equation

$$OCl^- + H_2O_2 \rightarrow Cl^- + H_2O + O_2$$

Ans. 31.96 g; 688.2 ml.

CHAPTER IX

PRECIPITATION ANALYSES

1. DETERMINATION OF SILVER

Method of Volhard

1 l of 0.1 N KCNS = Ag/10 = 10.79 g Ag

If alkali thiocyanate is added to a solution containing both silver and ferric ions, white, insoluble silver thiocyanate will form preferably and a *permanent* red coloration of ferric thiocyanate will not be obtained until practically all silver is precipitated:

$$CNS^- + Ag^+ \rightarrow \mathbf{AgCNS}$$
$$3CNS^- + Fe^{+++} \rightarrow [Fe(CNS)_3]$$

Requirements. 1. *Tenth-Normal Potassium (or Ammonium) Thiocyanate Solution.* As both these salts are hygroscopic and cannot be dried without decomposition, an exactly tenth-normal solution cannot be prepared by weighing out the solid salt. Dissolve approximately the right amount (about 10 g KCNS or 9 g NH_4CNS) in a liter of water.

2. *Ferric-Ammonium Alum Solution.* A cold, saturated solution of ferric alum to which enough nitric acid is added to cause the disappearance of the brown color. Use about 3.5 g of the alum, 10 ml of water, and 2 ml of 6 N HNO_3. Of this indicator use the same amount for all titrations, about 2–3 ml for 100 ml of the silver solution.

Standardization of Thiocyanate Solution

Weigh out portions of about 0.4 g of pure silver nitrate and dissolve in 100 ml of 0.3 N nitric acid. Add 2–3 ml of indicator solution and titrate with thiocyanate solution to a permanent red tint in the solution. Or dissolve 0.25-g portions of pure silver in 15 ml of 6 N nitric acid. Dilute to about 25 ml, boil till all nitrous fumes are expelled, add 75 ml of cold water and the indicator solution, and titrate with thiocyanate.

Determination of Silver in Silver Alloys

Dissolve 0.5 g of the brightly polished metal in 10 ml of 6 N nitric acid. After the silver has dissolved, dilute with 50 ml of water and boil to expel nitrous fumes.[1] Cool, add 2–3 ml of the ferric alum solution, and titrate with the thiocyanate solution as in the standardization. The presence of metals whose salts are colorless does not influence the accuracy of this determination, except that mercury must be absent because its thiocyanates are insoluble. Nickel and cobalt must not be present to any extent, because their salts are colored, and not more than 60 per cent of copper in an alloy is permissible. If more copper is present the following procedure must be used: Precipitate the silver by means of an excess of alkali thiocyanate, wash completely with water, place the funnel over an Erlenmeyer flask, break the apex of the filter, wash its contents into a flask by means of concentrated nitric acid, and heat the liquid to gentle boiling for three-quarters of an hour. As the sulfuric acid formed will have some influence upon the subsequent titration, dilute the solution with water to about 100 ml, and add a concentrated barium nitrate solution, drop by drop, until all the sulfuric acid is precipitated. Then titrate the silver with thiocyanate solution without filtering off the barium sulfate.

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[1] Nitrous acid reacts with thiocyanic acid, forming a red compound which may easily be mistaken for ferric thiocyanate.

2. DETERMINATION OF CHLORIDE

(*a*) Volhard's Method

1 l of 0.1 N $AgNO_3$ solution = Cl/10 = 3.546 g chlorine

According to Volhard's original directions, the chloride solution was treated with 0.1 N silver nitrate solution and then, without filtering off the precipitate, 2–3 ml of the ferric-ammonium alum solution was added and the excess of silver titrated with 0.1 N potassium or ammonium thiocyanate (see p. 147).

The results are satisfactory with large quantities of chloride, but in the titration of small quantities of chloride too high results are obtained, as was first shown by G. Drechsel[1] and later confirmed by M. A. Rosanoff and A. E. Hill.[2] Drechsel showed that it was impossible to get the true end point of the reaction, as the red coloration gradually disappeared on stirring, remaining permanent only after a considerable excess of thiocyanate had been added. The reason for this is that silver chloride is more soluble than silver thiocyanate. Thus the precipitate gradually reacts with the red ferric thiocyanate, as follows:

$$3\mathbf{AgCl} + Fe(CNS)_3 = 3\mathbf{AgCNS} + FeCl_3$$

Procedure. Weigh out accurately to four significant figures samples of about 0.2 g each. Dissolve in about 200 ml of water containing 5 ml of 6 N HNO_3. In other beakers, dissolve about 0.8-g portions of pure

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[1] *Z. anal. Chem.*, **16**, 351 (1877).

[2] *J. Am. Chem. Soc.*, **29**, 269.

$AgNO_3$, also weighed to four significant figures. Dissolve the $AgNO_3$ in about 50 ml of hot water and pour the silver nitrate solution slowly, while stirring, into the hot chloride solution. Wash the beakers well to remove all $AgNO_3$. Keep the solutions hot, but not quite boiling, until the silver chloride precipitate has coagulated sufficiently to be filtered. Filter off the precipitate, and wash the beakers and precipitate with at least 6 portions of hot water. In washing the precipitate on the filter, make sure that the upper edge of the paper is washed each time; if the filter paper fits the funnel tightly at the top, no precipitate will pass into the filtrate. Finally, to make sure that all the excess silver nitrate has been removed, test about 5 ml of fresh filtrate with a few drops of 6 N HCl; no precipitate of AgCl should form. Add ferric alum indicator solution and titrate with standardized thiocyanate solution.

The above procedure is equally applicable to the analysis of bromides, iodides, cyanides, and thiocyanates, all of which yield precipitates insoluble in dilute HNO_3. When the above procedure is followed it is not absolutely necessary to filter off the precipitate before titrating. The error is slight if the silver chloride precipitate is well coagulated.

Adsorption Indicators. Fajans and his collaborators[1] have shown that silver halide precipitates, owing to their colloidal properties, tend to adsorb excess Ag^+ or excess halogen ions from the solution with which they are in contact. The adsorbed Ag^+ has the property of dragging down with it the anions of certain organic dyestuffs, which are of a feebly acidic nature, and a change of color takes place as a result of the adsorption. Thus fluorescein in aqueous solution has a yellowish green color. When silver chloride is formed in the presence of a very slight excess of Ag^+, the anion of fluorescein is adsorbed and there is a change of color to reddish violet. If a very little of the indicator is present, the silver chloride precipitate assumes a reddish tint as soon as a very slight excess of Ag^+ is present.

In the titration of Cl^- with Ag good results are thus obtained in neutral solutions with fluorescein as indicator. To prepare the indicator solution, dissolve 0.2 g of the sodium salt of fluorescein in 100 ml of water or dissolve 0.2 g of fluorescein itself in 100 ml of alcohol. Use about 2 drops of indicator solution for each 10 ml of 0.1 N chloride solution to be titrated with 0.1 N silver nitrate solution. The results are accurate, even in the presence of considerable quantities of alkali cations, provided that the chloride solution is at least 0.005 N in halogen ions. Alkaline-earth cations interfere somewhat.

Bromides, iodides, and thiocyanates can be titrated in dilute solutions, even in the presence of dilute nitric acid, when eosin is chosen as the indicator. Two drops of the 0.5 per cent aqueous solution should be used for each 10 ml of 0.1 N halide to be titrated. The silver halide precipitate becomes red at the end point. Eosin cannot be used for the titration of chlorides with silver nitrate because the eosin is adsorbed and colors the silver chloride precipitate before the end point is reached. Fluorescein, on the other hand, can be used with chlorides, bromides, iodides, or thiocyanates.

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[1] *Z. physik. Chem.*, **97**, 478 (1921); **105**, 255 (1923); *Z. Electrochem.*, **29**, 495 (1923); *Naturwiss*, **11**, 165 (1923); *Z. anorg. allgem. Chem.*, **137**, 221 (1924).

In the titration of silver solutions, there are two ways in which an adsorption indicator can be used. An excess of standard halide solution can be added and the excess titrated with standard silver nitrate solution using fluorescein or eosin as indicator, or a slightly basic indicator can be used such as "rhodamine 6 G." In this case the cations of the indicator are adsorbed by the precipitate as soon as a slight excess of Br^- has been added and a color change takes place with the precipitate assuming a bluish violet hue. Nitric acid can be present during this titration with the basic indicator provided the concentration is not over 0.5 N in acid.

A number of other organic dyestuffs can be used as adsorption indicators. Thus Kolthoff[1] reports good results with "tropeolin yellow 00," "bromophenol blue," and "metanil yellow" in titrating dilute chloride solution with 0.1 N silver nitrate.

A Partial List of Adsorption Indicators for Volumetric Precipitations*

Titration of	Titrating Ion	Indicator	Notes
Cl^-	Ag^+	Dichlorofluorescein	$pH > 4$
Br^-	Ag^+	Eosin	$pH > 2$ Best in acetic acid solution
I^-	Ag^+	Eosin	Eosin is tetrabromofluorescein
SCN^-	Ag^+	Eosin	
CN^-	Ag^+	Diphenylcarbazide	
Ag^+	Br^-	Rhodamine 6 G	In 0.5 N HNO_3
OH^-	Pb^{++}	Fluorescein	Quite sharp in 0.01 and 0.1 N solutions
BO_2^- $B_4O_7^{=}$	Pb^{++}	Dichlorofluorescein	Accurate in neutral solution
$SO_4^{=}$	Pb^{++}	Dibromofluorescein	A better method is based on fractional precipitation†

* Pierce and Haenisch, *Quantitative Analysis.*

† See W. C. Schroeder, *Ind. Eng. Chem., Anal Ed.*, **5**, 403 (1933) and Sheen, Kahler and Cline, *ibid*, **9**, 69 (1937).

(*b*) Fr. Mohr's Method

If the neutral solution of an alkali chloride containing a few drops of potassium chromate solution is treated with silver nitrate solution, added from a buret, silver chloride is formed first, and any red precipitate of silver chromate disappears on stirring, on account of its reacting with chloride ions to form less soluble silver chloride.

$$Ag_2CrO_4 + 2NaCl = 2AgCl + Na_2CrO_4$$

When all the chloride is changed to insoluble silver chloride, the next drop of the silver solution will impart a permanent reddish color to the liquid. For small amounts of chloride in concentrated solutions this method gives very sharp results. If, however, the volume of the solution is too large, the results are not very accurate. A blank experiment must always be made to see how much of the silver solution is necessary to produce the red shade used in the titration when no chloride is present, and this amount must be deducted from that used in the analysis.

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[1] *Z. anal. Chem.*, **71**, 235 (1927).

Remark. If it is desired to titrate free hydrochloric acid, first neutralize the solution. With colorless chlorides having an acid reaction ($AlCl_3$), treat the solution with an excess of neutral sodium acetate solution and then titrate. With colored metal chlorides, precipitate the metal with caustic potash or sodium carbonate, filter, wash the precipitate, make the filtrate acid with acetic acid, and then titrate.

3. DETERMINATION OF CYANIDE. METHOD OF LIEBIG

1 l of 0.1 N $AgNO_3$ solution = KCN/5 = 13.02 g KCN

On adding silver nitrate solution, drop by drop, to a neutral or alkaline solution of an alkali cyanide, a white precipitate is formed when the two liquids first come in contact with one another, but on stirring it redissolves owing to the formation of potassium silver cyanide:

$$\mathbf{AgCN} + CN^- \rightarrow [Ag(CN)_2]^-$$

As soon as all the cyanide is transformed into the silver cyanide complex anion, the next drop of the silver solution will produce a permanent turbidity:

$$[Ag(CN)_2]^- + Ag^+ \rightarrow \mathbf{2AgCN}$$

The titration reaction is, therefore,

$$2CN^- + Ag^+ \rightarrow [Ag(CN)_2]^-$$

$1Ag^+$ corresponds to $2CN^-$, and the end point of the reaction is shown by the formation of a permanent precipitate as soon as more than $1Ag^+$ has been added for each $2CN^-$ ions.

Prepare the alkali cyanide solution in a beaker, add a little potassium hydroxide, and dilute to a volume of about 100 ml. Place the beaker on a piece of black glazed paper and titrate with constant stirring until the turbidity is obtained.

For the analysis of free hydrocyanic acid, add an excess of potassium hydroxide solution and treat as above.

The addition of 5 ml of 2 per cent potassium iodide solution slightly increases the sharpness of the end point in the above analysis. The precipitate then consists of silver iodide of which 1 molecule will dissolve in 2 molecules of potassium cyanide, just as silver nitrate does. The above precedure can be applied to any solution of alkali or alkaline-earth cyanide (the so-called *free cyanide*) but not to insoluble or complex cyanides.

4. DETERMINATION OF CHLORIDE, CYANIDE, AND THIOCYANATE ACIDS IN THE PRESENCE OF ONE ANOTHER

In one portion determine the free cyanide according to Liebig. To a second portion add an excess of 0.1 N silver solution, make acid with nitric acid, filter, wash the precipitate with water, and titrate the excess of silver in the filtrate according to Volhard. Pierce the filter containing the precipitate and transfer the latter by means of concentrated nitric acid to a flask and boil for three-quarters of an hour. By this means the cyanide and thiocyanate of silver go into solution, while the silver chloride remains undissolved. Dilute the solution to about 100 ml, add enough barium nitrate to precipitate the sulfuric acid formed, and titrate the silver corresponding to the cyanide and thiocyanate with potassium thiocyanate without filtering off the silver chloride or barium sulfate.

Computation. If t ml of 0.1 N $AgNO_3$ were used in the first titration, then $2t$ ml would be needed to precipitate all the cyanide. If T ml of 0.1 N $AgNO_3$ were required to precipitate all the cyanide, thiocyanate, and chloride, and t_1 ml of 0.1 N KCNS were used in the last titration, then

$$t \times 0.005202 = \text{g CN or } t \times 0.01302 = \text{g KCN}$$
$$(t_1 - 2t) \times 0.005808 = \text{g CNS or } (t_1 - 2t) \times 0.009718 = \text{g KCNS}$$
$$(T - t_1) \times 0.003546 \text{ g} = \text{Cl or } (T - t_1) \times 0.007456 = \text{g KCl}$$

5. DETERMINATION OF SULFURIC ACID BY BENZIDINE HYDROCHLORIDE[1]

$$1 \text{ l of } 0.1\ N \text{ NaOH} = H_2SO_4/20 = 4.904 \text{ g } H_2SO_4$$

Benzidine, $C_{12}H_8(NH_2)_2$, is a weak organic base. It forms stable salts with strong mineral acids, of which the sulfate is characterized by its slight solubility, particularly in water containing hydrochloric acid. The base itself is neutral toward phenolphthalein. The aqueous solutions of benzidine salts undergo hydrolysis and react as if the acid were free:

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[1] W. Müller, *Ber.*, **35**, 1587 (1902); Müller and Dürkes, *Z. anal. Chem.*, **42**, 477 (1903); F. Raschig, *Z. angew. Chem.*, **1903**, 617 and 818; von Knorre, *Chem. Ind.*, **28**, 2; and Friedheim and Nydegger, *Z. angew. Chem.*, **1907**, 9.

$$C_{12}H_8(NH_2)_2{\cdot}2HCl + 2OH^- \rightarrow 2Cl^- + C_{12}H_8(NH_2)_2 + 2H_2O$$

In other words, an aqueous solution of benzidine hydrochloride behaves like a mixture of hydrochloric acid and benzidine, and the amount of acid present may be titrated with alkali hydroxide, in the presence of phenolphthalein as indicator.

There are two methods which have been used for the volumetric estimation of sulfuric acid by means of benzidine. Müller treated the *neutral* solution of the sulfate with a solution of benzidine hydrochloride of known acidity.

$$C_{12}H_8(NH_2)_2{\cdot}2HCl + Na_2SO_4 = 2NaCl + \mathbf{C_{12}H_8(NH_2)_2{\cdot}H_2SO_4}$$

The precipitate of benzidine sulfate was filtered off and the filtrate titrated with a standard solution of alkali. The loss in acidity corresponded to the amount of sulfuric acid present. Raschig, on the other hand, recommends treating the neutral or acid solution of the sulfate with benzidine hydrochloride solution, filtering off the precipitated benzidine sulfate, washing it, and then suspending it in water and titrating the sulfuric acid with 0.1 *N* sodium hydroxide at 50°.

Raschig prepares the reagent as follows: Triturate 40 g of benzidine with 40 ml of water and rinse the paste into a liter measuring flask with about 750 ml of water. Add 50 ml of concentrated hydrochloric acid and dilute to the mark. Shake well. Soon the benzidine will all dissolve, forming a brown solution which may be filtered if necessary. To use as a reagent, dilute with 19 times as much water.

Procedure. To the neutral or slightly acid solution of the sulfate, containing not more than 0.1 g of sulfate anions per 50 ml of solution, add the diluted benzidine solution in the cold, using 150 ml for each 0.1 g of sulfate ions. A crystalline precipitate of benzidine sulfate forms at once, which can be filtered as follows after standing 5 minutes.

Place a Witt perforated porcelain plate in a funnel of 200-ml capacity. The diameter of the plate should be about 40 mm on the top. Place two pieces of filter paper on this plate, about 46 mm in diameter. Insert the funnel in a rubber stopper and place in a suction bottle. Moisten the filters with water, apply gentle suction, and press the papers to the sides of the funnel so that a tight pad is formed of about 3-mm depth, which will not allow precipitate to get by. Pour the supernatant liquid through this filter, rinse the precipitate and mother liquor into the funnel, and drain. Wash with 15 ml of water added in small portions. Place the precipitate and filter, without the porcelain plate, in an Erlenmeyer flask, add 50 ml of water, and shake the contents of the stoppered flask until a homogeneous paste is obtained. Remove the rubber stopper from the flask, rinse off with water, add a drop of phenolphthalein solution, heat to about 50°, and titrate with 0.1 *N* sodium hydroxide. When the end point is nearly reached, boil the liquid for 5 minutes, and then finish the titration.

Remark. The method does not give good results in the presence of ferric salts, but this difficulty can be overcome by reducing the ferric ion with hydrazine hydrochloride. Not more than 10 moles of HCl, 15 moles HNO_3, 20 moles $HC_2H_3O_2$, 5 moles alkali salt, or 2 moles ferric iron should be present to 1 mole of H_2SO_4. A satisfactory determination of the sulfur in pyrite can be made by dissolving 0.5 g of the sample according to the Lunge method (see Pyrite), evaporating off the nitric acid, taking up the residue in a little hydrochloric acid, diluting to 500 ml and using 100 ml for the treatment with benzidine hydrochloride.

6. DETERMINATION OF SULFURIC ACID (HINMAN)[1]

$$1 \text{ l of } 0.1\ N\ Na_2S_2O_3 = H_2SO_4/30 = 98.08/30 = 3.269 \text{ g } H_2SO_4$$

This method depends upon the fact that barium chromate is easily dissolved by dilute hydrochloric acid whereas barium sulfate is not; 1 l of cold water dissolves about 2 mg of $BaSO_4$ and 3 mg of $BaCrO_4$, but the latter salt dissolves easily in acid because $HCrO_4^-$ as an acid is comparable to H_2CO_3. If a solution of barium chromate in dilute hydrochloric acid is added in slight excess to a solution containing SO_4^{--} ions, $BaSO_4$ is precipitated; then upon neutralizing the solution the remainder of the barium is precipitated as $BaCrO_4$, leaving 1 mole of CrO_4^{--} in solution for each mole of SO_4^{--} originally present. After filtering, the dissolved chromium can be determined iodimetrically (p. 133).

The method is rapid and capable of giving theoretical values in the analysis of sulfates containing less than 5 per cent of SO_3. By slightly varying the conditions, however, the results are influenced and the most favorable conditions are not always the same for different sulfates. The method, therefore, is suitable for routine work, but is not theoretically perfect.[2]

The results are likely to be high if the barium chromate contains any water-soluble chromate. Since the solubility of barium chromate in hot water is appreciable there will always be a positive error from this source, if the solution is filtered hot.

The results will be low: (1) If there is any reduction of chromate other than the desired reduction with iodide; this may be caused by the presence of too much hydrochloric acid during the first precipitation. (2) If any other chromate is precipitated with the barium chromate, such as basic ferric chromate. (3) If the solution is not acid enough during the treatment with iodide, incomplete reduction may result. (4) If the solution is hot, or contains an insufficient amount of iodide, some loss of the iodine may take place.

Prepare the barium chromate reagent by precipitating barium chloride with potassium chromate at the boiling temperature. Wash the precipitate with hot, dilute acetic acid and then with water till free from chromate. Dissolve 2–4 g of the dry salt in 1 l of normal hydrochloric acid. One milliliter should precipitate 0.63–1.3 mg of SO_3.

Procedure. If the solution of the sulfate is acid, nearly neutralize it with alkali hydroxide solution. Dilute with water until not more than about 5 mg of SO_3 is present in 100 ml. Heat to boiling and slowly add a slight excess of the barium chromate reagent. Boil for 1 minute, or for 5 minutes if any carbonate was present.

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[1] *Am. J. Sci. and Arts*, **114**, 478 (1877). Cf. Andrews, *Am. Chem. J.*, **2**, 567; Pennock and Morton, *J. Am. Chem. Soc.*, **1903**, 2265; Bruhns, *Z. anal. Chem.*, **45**, 573 (1906); Holliger, *ibid.*, **19**, 84 (1910), and M. Reuter, *Chem. Ztg.*, **1898**, 357.

[2] In some cases it is simplest to apply a correction factor. Thus Komarowsky, *Chem. Ztg.*, **31**, 498 (1907), deducts 0.3 ml from the final buret reading.

To the boiling solution cautiously add pure $CaCO_3$ in small portions until present in slight excess (use ammonia if iron, nickel, or zinc is present). Cool to room temperature and dilute to the mark in a 250-ml measuring flask. Mix thoroughly by pouring back and forth several times into a beaker which is dry at the start, filter through a dry filter, reject the first 20 ml and take 100 ml of the filtrate for the titration.

Add 2–3 g of potassium iodide and 10 ml of concentrated hydrochloric acid. Shake well and allow to stand 15 minutes. Then titrate slowly with 0.02 N sodium thiosulfate solution.

Remark. When iron, nickel, or zinc salts are contained in the solution, the acid present cannot be neutralized with calcium carbonate, because these salts when boiled with calcium carbonate and a soluble chromate form insoluble basic chromates, so that too little chromic acid will be found in the filtrate corresponding to too little sulfuric acid. In such a case the neutralization is effected with ammonia, an excess being added, the solution boiled until the excess is almost entirely expelled and then filtered.

HOME PROBLEMS

80. Compute the percentage of silver in an alloy from the following data: weight of alloy = 0.4665 g; used 34.85 ml of KCNS solution of which 1 ml = 0.0188 g of pure $AgNO_3$.

81. What weight of silver alloy should be taken for analysis so that the milliliters 0.045 N KCNS solution multiplied by 2 will give the percentage of Ag present?

82. A silicate weighing 2.000 g yields 0.2558 g of NaCl and KCl which is dissolved and treated with 35 ml of $N/10$ silver solution. The excess of the latter reacts with 0.92 ml of $N/50$ thiocyanate solution. Find percentage of Na_2O and of K in the silicate.

83. Find the weights of dissolved KCl, KCN, KCNS in 500 ml of solution which is analyzed as follows: 30 ml reacts in the Liebig method with 9.57 ml of a solution containing 16 mg of $AgNO_3$ per milliliter. Then 75 ml more of Ag solution is added, the precipitate of AgCl, AgCNS, and AgCN removed, and the excess Ag titrated with 9.5 ml of $N/10$ KCNS solution. The above precipitate is treated with HNO_3 and Ba nitrate solution. The resulting solution containing all the silver except that of the AgCl reacts with 58.40 ml of $N/10$ KCNS solution.

84. What volume of thiosulfate, of which 1 ml is equivalent to 0.00583 g of Cu in Low's iodide method, will react with the iodine set free by 9 ml of the same H_2O_2 solution? $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$.

85. If by the passage of 2 cu ft of illuminating gas at 20° and 750 mm pressure through Br water, enough H_2SO_4 is formed so that 34 ml of 0.04 N thiosulfate are used in the Hinman method, what percentage by volume of H_2S does the illuminating gas contain if all the S comes from this compound?

86. If pyrite, FeS_2, is analyzed by the benzidine hydrochloride method, after oxidation of all the sulfide to sulfate, what volume of 0.08965 N NaOH solution will be required in the analysis of 0.28 g of a sample containing 44.00 per cent sulfur?

CHAPTER X

GRAVIMETRIC ANALYSIS. GENERAL PRINCIPLES

Gravimetric analysis, or analysis by weight, is the name given to methods in which one of the products, obtained from the decomposition of a weighed sample, is weighed. The commonest type of gravimetric methods is that in which a precipitate is formed in a solution, separated from the solution and its dissolved substances by filtration, and weighed after suitable drying. The principles involved in precipitation and filtration are the same as those of qualitative analysis; as a matter of fact, most of the reactions used in qualitative analysis can be utilized in quantitative work. Let us review briefly some of the things learned in qualitative analysis concerning the solubility relations.

A substance like potassium nitrate on being brought into contact with water at once begins to dissolve. The rate of solution is influenced somewhat by the amount of surface exposed by the salt, a fine powder dissolving more rapidly than a single large crystal. At first the substance dissolves quite rapidly, particularly if the liquid is kept stirred, but gradually the speed slackens, and finally a time comes when the water at a given temperature will dissolve no more of the salt. The solution is then said to be *saturated* with the salt; it makes no difference how much potassium nitrate is available in excess of the amount required to form a saturated solution, the solution when once saturated at any temperature will dissolve no more salt.

The quantity of salt required to form a saturated solution varies with the temperature, more so with potassium nitrate than with many other salts. At 0° the saturated solution contains only 1.3 moles of potassium nitrate, whereas 2.7 moles dissolve at 20° and 25 moles dissolve at 100°.

If a solution containing 5 moles of potassium nitrate is prepared by dissolving the salt in hot water and the solution is then cooled to 20°, we obtain what is called a *supersaturated* solution. A state of supersaturation can be maintained for some time provided that care is taken not to disturb the solution in any way. If the supersaturated solution is agitated, or, better, if a tiny fragment of potassium nitrate is thrown into it, crystallization starts and continues until finally the solution contains only 2.7 moles of the salt, which is the quantity of potassium nitrate required to form a saturated solution at 20°.

The solubility of a substance at any temperature is usually determined by two methods: first, by shaking up the salt with water until a saturated solution is obtained; second, by forming a supersaturated solution and allowing the excess of the salt to crystallize out. Usually the values obtained by the former method are a little lower than those obtained by the latter method; a slightly undersaturated solution is obtained in the first case and a slightly supersaturated one in the other.

When a solution of potassium nitrate is brought into contact with more of the salt, whether more of the salt will dissolve or not is determined solely by the concentration of the solution. If it is already saturated with potassium nitrate, no more of the salt will dissolve; if unsaturated, more salt will dissolve to form a saturated solution. The equilibrium between a liquid and a solid which is soluble in it is determined solely by the concentration of the solution.

Chemists prefer to look upon a state of equilibrium as a condition of dynamic equilibrium rather than as one of static equilibrium. Instead of thinking of the saturated solution of potassium nitrate as one which has no tendency to dissolve more potassium nitrate, it is preferable to consider the solution as one in which the tendency to precipitate potassium nitrate is exactly balanced by the tendency to dissolve potassium nitrate. When the solution is undersaturated and more salt is available, the tendency to dissolve is greater than the tendency to precipitate; and when the solution is supersaturated the tendency to precipitate is greater than the tendency to dissolve.

The equilibrium principle is the same in respect to difficultly soluble substances. It requires only 0.0015 g (= 0.01 millimole) of silver chloride to form a saturated solution in 1 l of water. If more than this quantity of silver chloride is produced as a result of a chemical reaction in an aqueous solution, the solution is supersaturated and the excess silver chloride will be precipitated very quickly as a rule.

Chemical Equilibrium and the Mass-Action Law

If hydrogen sulfide gas is passed into a solution containing zinc chloride, a white precipitate of zinc sulfide is formed:

$$ZnCl_2 + H_2S = \mathbf{ZnS} + 2HCl$$

If the precipitate of zinc sulfide is filtered off and treated with hydrochloric acid it will dissolve:

$$\mathbf{ZnS} + 2HCl = ZnCl_2 + H_2S$$

Similarly, the addition of ammonium carbonate to a solution of calcium chloride in water causes the formation of a white precipitate of calcium carbonate:

$$CaCl_2 + (NH_4)_2CO_3 = \mathbf{CaCO_3} + 2NH_4Cl$$

The precipitate can be dissolved, however, by boiling it with ammonium chloride solution.

In each of the above reactions there are evidently two opposing tendencies — the tendency of zinc sulfide to precipitate and its tendency to dissolve; the tendency of calcium carbonate to precipitate and its tendency to dissolve. To express the fact that the reaction may go in either direction it is customary to write the symbols separated by a double arrow instead of by an equality sign:

$$ZnCl_2 + H_2S \rightleftarrows \mathbf{ZnS} + 2HCl$$
$$CaCl_2 + (NH_4)_2CO_3 \rightleftarrows \mathbf{CaCO_3} + 2NH_4Cl$$

Such reactions are called *reversible.* It was once thought that reversible reactions were of rare occurrence, but it is now customary to consider all chemical reactions reversible, although many reactions, especially most of those used in analytical chemistry, go so completely in one direction that only a negligible quantity of one or more of the initial substances remains unchanged. In general, when two substances A and B react at a constant temperature to form C and D, then, to some extent at least, C and D react to form A and B, and equilibrium is reached when the ratio of the product of the concentrations of A and B to the product of the concentrations of C and D has a definite, constant value. This value is characteristic of the equilibrium between the compounds involved.

The above reaction may be expressed as follows:

$$A + B \rightleftarrows C + D$$

in which A, B, C, and D represent four different substances reacting in the molecular proportions indicated by their symbols. The final equilibrium is expressed by the mathematical equation:

$$\frac{[C]}{[A]} \times \frac{[D]}{[B]} = k$$

in which $[A]$, $[B]$, $[C]$, and $[D]$ represent the final concentrations[1] of the four reacting substances and k is some definite number called the equilibrium constant. The value k varies with the temperature.

If more than one molecule of substance takes part in the reaction, the conditions are somewhat more complicated. This is expressed by the general equation

$$mA + nB \rightleftarrows pC + qD$$

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[1] Concentrations in such cases are usually expressed in *moles per liter.*

and the final equilibrium is expressed mathematically

$$\frac{[C]^p \times [D]^q}{[A]^m \times [B]^n} = k$$

in which $[A]$, $[B]$, $[C]$, and $[D]$ represent, as before, the concentrations when equilibrium is reached.

This is the so-called *law of mass action*, which was discovered by Guldberg and Waage in 1867. It is to be noted that it is the concentrations, or masses present in a unit of volume, rather than the actual masses of the substances, which find expression in this law.

This law applies to a state of *homogeneous equilibrium*. A homogeneous system is one in which every part of it is like every other part. A mixture of two solid substances is not homogeneous. A solution, on the other hand, is homogeneous when it is thoroughly mixed, as it is impossible to distinguish any difference between different portions of the solution. Similarly a mixture of gases represents a homogeneous system. Such homogeneous systems are called *phases*. A mixture of a solid, a solution, and a gas represents three phases; two solids, two phases; two immiscible liquids, two phases.

In the reactions between zinc chloride and hydrogen sulfide and between calcium chloride and ammonium carbonate, a precipitate was formed in each reaction. The mass-action law applied only to the zinc sulfide and to the calcium carbonate that remained in solution. The fact that these substances are only very slightly soluble in water favors the progress of the reaction in the direction by which these substances are formed. The mass-action law shows that, when the concentration of any substance participating in a chemical reaction is increased, the tendency for the reaction to take place in the direction by which this substance is decomposed is increased; when any substance formed by means of a chemical reaction is removed, the tendency for the reaction to proceed in the direction by which this substance is formed is increased. The formation of a precipitate or the escape of a gas, as fast as the substance is formed by means of a chemical reaction, tends to make the reaction take place more completely. If all the gas is boiled off, the reaction by which it is formed will take place completely. Similarly, if any precipitate were absolutely insoluble in water, the reactions by which this substance is formed would take place completely.

Solubility Product

Silver chloride is slightly soluble in water; 0.00001 mole (1.5 mg) of the solid dissolves in 1 l of the solvent. When water is placed in contact with an excess of silver chloride, a state of equilibrium is soon reached between the solid and the solution. If more than this quantity of dissolved substance is present at any time, the solution is supersaturated and tends to precipitate silver chloride; if less, then more silver chloride will be dissolved. When equilibrium is reached the tendency of the salt to precipitate is equal to the tendency of the salt to dissolve.

The dissolved silver chloride also exists in a state of equilibrium between the ionogen and the ions. This equilibrium apparently takes place almost instantly, whereas the equilibrium between the solid and the solution is established more slowly. For all concentrations of such a slightly soluble substance as silver chloride, it is fair to assume that the mass-action law holds rigidly. Applied to the reaction

$$AgCl \rightleftarrows Ag^+ + Cl^-$$

and denoting the concentration of the dissolved, non-ionized silver chloride as [AgCl], of silver ions as [Ag], and of chlorine ions as [Cl], the law is expressed as follows:

$$\frac{[Ag] \times [Cl]}{[AgCl]} = k$$

In this equation k has a definite value, called the *ionization constant*, which varies with the temperature but has otherwise a definite value for every substance. The concentrations are expressed in moles per liter; cf. p. 34. When the solution is saturated with silver chloride the value of both numerator and denominator has reached the saturation value. If the value of [AgCl] is greater than this saturation value, the solution is supersaturated and is no longer in equilibrium with undissolved solid. The value [AgCl] is extremely small and cannot be measured accurately because the small quantity of silver chloride that dissolves is almost, if not quite, completely ionized. It is more convenient to use the ion concentration product [Ag] × [Cl], which reaches its maximum value when the solution is saturated; it is called the *solubility product* of silver chloride. In general, if the substance $A_m B_n$ ionizes into mA and nB ions, the solubility product, S_p, is found by the equation:

$$S_p = [A]^m \times [B]^n$$

Whenever a substance which has a very small solubility product is formed by means of a chemical reaction, the greater part of the substance will leave the solution in the form of a precipitate and the reaction will go practically to completion. The table on p. 162 shows that the saturated solution of silver chloride contains only about one hundred-thousandth of a mole (= 0.01 millimole) of solid salt per liter. The table also shows that when the product obtained by multiplying the concentration of the silver ions by the product of the concentration of the chloride ions in any aqueous solution is equal to 1.2×10^{-10} the solution is saturated with silver chloride. By adding an excess of chloride ions to a solution containing silver ions, it is possible, therefore, to precipitate practically all the silver. It is evident that it will take fewer silver ions to give the solubility product when an excess of chloride ions is used than when pure silver chloride is dissolved in water.

The precipitated silver chloride will dissolve completely in potassium cyanide, because the silver ion forms with the cyanide ion a complex which is ionized to such a slight extent that the solubility product of silver chloride is no longer reached, even although all the chlorine is present as chloride ions.

Experience has shown that the conditions are somewhat more complicated in concentrated solutions such as are obtained with the very soluble substances. In future discussion, therefore, the solubility will be expressed, as a rule, in terms of the solubility product only when the substance does not dissolve to a greater extent than 0.01 mole per liter. In such dilute solutions the ionization of salts is nearly 100 per cent. It is therefore logical, under such conditions, to express the solubility in terms of the ions, whereas with very soluble substances it is better to measure the solubility in terms of the mass of dissolved substance.[1]

In the accompanying table the solubility of the substance is expressed in three ways: in grams of dissolved substance per liter; in moles per liter; and, finally, in terms of the solubility product, using moles per liter. The solubility of most of the substances given in the table is so slight that the quantity dissolved is negligible for most purposes. Whenever the word *insoluble* is used in this book it is with the understood limitation that no substance is absolutely insoluble in water.

This table is prepared from many sources, and some of the values are based upon solubility determinations by methods which are now considered inaccurate. The table gives a good idea of the relative order of magnitude, however. For copper sulfide, the table states that 8.8×10^{-21} g dissolves in 1 l of water. Obviously, the experimental determination of such a small value is fraught with difficulty and the probable error is large. For most purposes such a value represents a negligible quantity and the statement is often made that copper sulfide is insoluble in water. It is instructive, however, to compare the solubility products of the various sulfides, and important methods of separation have been based upon such studies. Only two significant figures have been given in the table, although it is obvious that more

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[1] Cf. K. G. Denbigh, *J. Chem. Education*, **18**, 126 (1941).

SOLUBILITIES AND SOLUBILITY PRODUCTS AT ROOM TEMPERATURE

Substance	Solubility in Grams per Liter	Solubility in Moles per Liter	Solubility Product
$AgBr$	1.1×10^{-4}	5.9×10^{-7}	$[Ag]\times[Br]=3.5\times10^{-13}$
$Ag_2(CN)_2$	4.3×10^{-5}	1.6×10^{-7}	$[Ag]\times[Ag(CN)_2]=2.6\times10^{-14}$
$AgCNS$	1.4×10^{-4}	8.4×10^{-7}	$[Ag]\times[CNS]=7.1\times10^{-13}$
$AgCl$	1.5×10^{-3}	1.1×10^{-5}	$[Ag]\times[Cl]=1.2\times10^{-10}$
Ag_2CrO_4	2.5×10^{-2}	7.5×10^{-5}	$[Ag]^2\times[CrO_4]=1.7\times10^{-12}$
$Ag_2Cr_2O_7$	8.3×10^{-2}	1.9×10^{-4}	$[Ag]^2\times[Cr_2O_7]=2.7\times10^{-11}$
Ag_2O	2.1×10^{-2}	9.0×10^{-5}	$[Ag]\times[OH]=1.9\times10^{-8}$
AgI	3.0×10^{-6}	1.3×10^{-8}	$[Ag]\times[I]=1.7\times10^{-16}$
$AgIO_3$	4.4×10^{-2}	1.5×10^{-4}	$[Ag]\times[IO_3]=2.3\times10^{-8}$
Ag_3PO_4	6.5×10^{-3}	1.6×10^{-5}	$[Ag]^3\times[PO_4]=1.8\times10^{-18}$
Ag_2SO_4	8.0	2.6×10^{-2}	$[Ag]^2\times[SO_4]=7.0\times10^{-5}$
$BaCO_3$	1.3×10^{-2}	4.3×10^{-5}	$[Ba]\times[CO_3]=1.9\times10^{-9}$
$BaCrO_4$	3.8×10^{-3}	1.5×10^{-5}	$[Ba]\times[CrO_4]=2.3\times10^{-10}$
$BaSO_4$	2.5×10^{-3}	1.1×10^{-5}	$[Ba]\times[SO_4]=1.2\times10^{-10}$
BaF_2	1.3	7.5×10^{-3}	$[Ba]\times[F]^2=1.7\times10^{-6}$
$CaCO_3$	1.3×10^{-2}	1.3×10^{-4}	$[Ca]\times[CO_3]=1.7\times10^{-8}$
CaC_2O_4	8.0×10^{-3}	6.2×10^{-5}	$[Ca]\times[C_2O_4]=3.8\times10^{-9}$
$CaCrO_4$	23.	1.5×10^{-1}	$[Ca]\times[CrO_4]=2.3\times10^{-2}$
CaF_2	1.6×10^{-2}	2.0×10^{-4}	$[Ca]\times[F]^2=3.2\times10^{-11}$
$CaSO$	2.0	1.5×10^{-2}	$[Ca]\times[SO_4]=2.3\times10^{-4}$
$Cu_2(CNS)_2$	5.0×10^{-4}	2.1×10^{-6}	$[Cu]\times[CNS]=1.7\times10^{-11}$
Cu_2Cl_2	1.2×10^{-1}	6.0×10^{-4}	$[Cu]\times[Cl]=1.4\times10^{-6}$
Cu_2I_2	3.0×10^{-4}	8.0×10^{-7}	$[Cu]\times[I]=2.6\times10^{-12}$
CuS	8.8×10^{-21}	9.2×10^{-23}	$[Cu]\times[S]=8.5\times10^{-45}$
CdS	8.6×10^{-13}	6.0×10^{-15}	$[Cd]\times[S]=3.6\times10^{-29}$
$Fe(OH)_2$	1.4×10^{-3}	1.6×10^{-5}	$[Fe]\times[OH]^2=1.6\times10^{-14}$
FeS	3.4×10^{-8}	3.9×10^{-10}	$[Fe]\times[S]=1.5\times10^{-19}$
$Fe(OH)_3$	4.8×10^{-8}	4.5×10^{-10}	$[Fe]\times[OH]^3=1.1\times10^{-36}$
Hg_2Br_2	3.9×10^{-5}	6.9×10^{-8}	$[Hg_2]\times[Br]^2=1.3\times10^{-21}$
Hg_2Cl_2	3.8×10^{-4}	8.0×10^{-7}	$[Hg_2]\times[Cl]^2=2.0\times10^{-18}$
Hg_2I_2	2.0×10^{-7}	3.1×10^{-10}	$[Hg_2]\times[I]^2=1.2\times10^{-28}$
HgO	3.2×10^{-7}	1.5×10^{-9}	$[Hg]\times[OH]^2=1.4\times10^{-26}$
HgS	1.5×10^{-24}	6.3×10^{-27}	$[Hg]\times[S]=4.0\times10^{-53}$
K_2PtCl_6	11.	2.3×10^{-2}	$[K]^2\times[PtCl_6]=4.9\times10^{-5}$
$MgCO_3$	4.3×10^{-1}	5.1×10^{-3}	$[Mg]\times[CO_3]=2.6\times10^{-5}$
$Mg(OH)_2$	1.2×10^{-2}	2.0×10^{-4}	$[Mg]\times[OH]^2=3.4\times10^{-11}$
$MgNH_4PO_4$	8.6×10^{-3}	6.3×10^{-5}	$[Mg]\times[NH_4]\times[PO_4]=2.5\times10^{-13}$
$Mn(OH)_2$	....	....	$[Mn]\times[OH]^2=4.0\times10^{-14}$
MnS	3.3×10^{-6}	3.8×10^{-8}	$[Mn]\times[S]=1.4\times10^{-15}$
NiS least soluble allotropic form	7.0×10^{-11}	1.2×10^{-12}	$[Ni]\times[S]=1.4\times10^{-24}$
$PbBr_2$	9.7	2.7×10^{-2}	$[Pb]\times[Br]^2=7.9\times10^{-5}$
$PbCl_2$	11.	3.9×11^{-2}	$[Pb]\times[Cl]^2=2.4\times10^{-4}$

SOLUBILITIES AND SOLUBILITY PRODUCTS AT ROOM TEMPERATURE — *Continued*

Substance	Solubility in Grams per Liter	Solubility in Moles per Liter	Solubility Product
$PbCO_3$	1.1×10^{-3}	4.1×10^{-6}	$[Pb]\times[CO_3]=1.7\times10^{-11}$
PbI_2	$6\ 8\times10^{-1}$	1.5×10^{-3}	$[Pb]\times[I]^2=1.4\times10^{-8}$
$Pb_3(PO_4)_2$	1.4×10^{-4}	1.7×10^{-7}	$[Pb]^3\times[PO_4]^2=1.5\times10^{-32}$
$PbSO_4$	4.2×10^{-2}	1.5×10^{-4}	$[Pb]\times[SO_4]=2.3\times10^{-8}$
$PbCrO_4$	4.3×10^{-5}	1.3×10^{-7}	$[Pb]\times[CrO_4]=1.8\times10^{-14}$
PbS	4.9×10^{-12}	2.0×10^{-14}	$[Pb]\times[S]=4.2\times10^{-28}$
SrC_2O_4	6.6×10^{-2}	3.8×10^{-4}	$[Sr]\times[C_2O_4]=1.4\times10^{-7}$
$SrCO_3$	1.0×10^{-2}	6.8×10^{-5}	$[Sr]\times[CO_3]=4.6\times10^{-9}$
SrF_2	2.3×10^{-1}	1.8×10^{-3}	$[Sr]\times[F]^2=2.5\times10^{-9}$
$SrSO_4$	1.1×10^{-1}	6.0×10^{-4}	$[Sr]\times[SO_4]=3.6\times10^{-7}$
$TlBr$	4.8×10^{-1}	1.7×10^{-3}	$[Tl]\times[Br]=2.9\times10^{-6}$
$TlCNS$	3.2	1.2×10^{-2}	$[Tl]\times[CNS]=1.4\times10^{-4}$
$TlCl$	3.4	1.4×10^{-2}	$[Tl]\times[Cl]=2.0\times10^{-4}$
TlI	6.4×10^{-2}	1.9×10^{-4}	$[Tl]\times[I]=3.6\times10^{-8}$
$Zn(OH)_2$	6.1×10^{-5}	6.3×10^{-7}	$[Zn]\times[OH]^2=1.8\times10^{-14}$
ZnS	3.3×10^{-10}	3.5×10^{-12}	$[Zn]\times[S]=1.2\times10^{-23}$

would be justifiable for the more soluble substances, while even the first figure is doubtful for the very insoluble substances. The values are affected to different degrees by changes in temperature and the presence of other substances in solution. A careful, critical study of all the experimental data would be necessary to give the proper number of significant figures, and it would be necessary to give the exact temperature.

In computing the solubility products, the assumption has been made that the ionization is complete and no attention has been paid to the effect of hydrolysis.

Two examples will be given to illustrate the method of computing the molar solubility, S_m, and the solubility product, S_p. A saturated solution of silver iodide contains 3.0×10^{-6} g (= 0.0030 mg) per liter. The molecular weight of silver iodide is 234.8. The saturated solution, therefore, contains $3.0 \times 10^{-6} \div 235 = 1.3 \times 10^{-8}$ mole. At this dilution the dissolved silver iodide can be assumed to be completely ionized:

$$AgI \rightleftarrows Ag^+ + I^-$$

and, since 1 mole of silver iodide furnishes 1 mole of silver ions and 1 mole of iodine ions, it is evident that the solubility product, S_p, is for $[Ag] \times [I] = [1.3 \times 10^{-8}] \times [1.3 \times 10^{-8}] = 1.7 \times 10^{-16} = S_p$.

A saturated solution of silver phosphate contains 6.5×10^{-3} g (= 6.5 mg) per liter. The substance is much more soluble in water than silver iodide, but its solubility product is smaller. The molecular weight of silver phosphate is 418.7. The saturated solution, therefore, contains $6.5 \times 10^{-3} \div 419 = 1.6 \times 10^{-5}$ mole of silver phosphate, which can be assumed to be completely ionized:

$$Ag_3PO_4 \rightleftarrows 3Ag^+ + PO_4^{---}$$

One mole of silver phosphate yields 3 moles of silver[1] and 1 mole of phosphate ions. The solubility product is

$$[Ag]^3 \times [PO_4] = [3 \times 1.6 \times 10^{-5}]^3 \times [1.6 \times 10^{-5}] = 1.8 \times 10^{-18} = S_p$$

Expressing this in terms of the solubility product, we may say that precipitation results when the solubility product is exceeded. Therefore, by increasing the concentration of the precipitant, say Ag^+, the quantity of other ion, say Cl^-, required to furnish a precipitate is diminished and the precipitation is more complete. For practical purposes, a reaction is complete or *quantitative,* as we often say, when less than 0.1 mg remains in solution. A large excess of reagent, however, usually does more harm than good. In many cases the precipitate is more soluble in a large excess of reagent. Thus barium sulfate is least soluble in dilute sulfuric acid but after a certain concentration is reached the solubility increases and the precipitate dissolves readily in hot, concentrated sulfuric acid. The most common effect, however, is to diminish the purity of the precip-

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[1] If x moles of Ag_3PO_4 dissolve in a liter of water and the Ag_3PO_4 is completely ionized, the concentration of the Ag^+ is $3x$ and that of the PO_4^{---} is x when the concentration is expressed in *moles per liter.* If the concentration is expressed in *equivalents per liter* (i.e., in terms of *normal* solutions), the x moles of Ag_3PO_4 furnish $3x$ equivalents of Ag_3PO_4 which ionize into $3x$ equivalents of Ag^+ and $3x$ equivalents of PO_4^{---}. The mass-action law expression $[Ag]^3 \times [PO_4]/[Ag_3PO_4] = k$ holds for either method of expressing concentrations, but it is, on the whole, simplest and best to express solubility products in *moles per liter,* and $[Ag]^3 \times [PO_4] = 27x^4$ in a saturated solution of silver phosphate containing x molecules of dissolved silver phosphate completely ionized. From the solubility product, the quantity of dissolved substance can be calculated. As one of the more complicated cases, let us consider lead phosphate. The solubility product, $[Pb]^3 \times [PO_4]^2$, is 1.5×10^{-32}. If x moles of $Pb_3(PO_4)_2$ dissolve in a liter of water and the salt is completely ionized, the solution will contain $3x$ moles of Pb^{++} and $2x$ moles of PO_4^{---} and

$$[Pb]^3 \times [PO_4]^2 = [3x]^3 \times [2x]^2 = 1.5 \times 10^{-32}$$

or

$$108x^5 = 1.5 \times 10^{-32} = 1500 \times 10^{-35}$$
$$x = 1.7 \times 10^{-7}$$

Solved with the aid of logarithms (cf. p. 47).

In applying the solubility-product principle it must be remembered that hydrolysis often takes place when the salt dissolves in water. In such circumstances the above methods of computation should be modified.

itate. The precipitate in forming may entrap some of the solution, an *inclusion error;* or some of the soluble ions may stick to the surface of the precipitate, *occlusion or adsorption.*

Colloidal Solutions

When a precipitate forms from a dilute solution, its particles are often very small. In estimating the dimensions of small particles, such as molecules, ions, or finely divided matter in suspension, it is customary to use three linear units: the *micron* = 10^{-6} meter = 10^{-3} mm = 1 μ, the *millimicron* = 10^{-6} mm = 1 mμ and the *Ångström* = 10^{-7} mm = 0.1 mμ = 1 Å. For very small weights the unit γ (gamma) is used, representing 0.001 mg. Some writers have used the symbol $\mu\mu$ for the millimicron, but this practice is likely to lead to confusion; it is better to reserve the letter " m " for one-thousandth and the Greek μ (mu) for one-millionth of a millimeter.

A very large molecule, such as that of starch, when dissolved in water has particles which may be 5 mμ in diameter but the solution shows some of the properties of colloids. In general, molecules in aqueous solution are rarely larger than 1 mμ in diameter, and the ions, although hydrated, are rarely larger than a few angstroms in diameter. If an aqueous solution of an electrolyte is illuminated by a powerful beam of light, there is no scattering of the light rays when the solution is viewed at right angles to the direction of the beam; the solutions are optically " empty " and show nothing when viewed under the ultramicroscope. If particles larger than 100 A (= 10 mμ) are present, they will scatter the light and thus become visible under the ultramicroscope by the so-called *Tyndall effect.*

A solution may appear clear to the naked eye although the particles have much larger than molecular dimensions. Thus, if hydrogen sulfide is passed through a solution of arsenic trioxide, the liquid will become orange in color but it will appear clear if held up before the eye. Under the ultramicroscope myriads of bright particles will be observed in rapid motion, and, if the liquid is placed in a strong beam of light, a marked scattering of the light rays will be noticed. With the ultramicroscope, the presence of particles larger than 10 mμ can be detected. With the ordinary microscope, the limit is about 0.25 μ.

If the particles of a *solute* (substance dissolved) present in a solvent are smaller than 1 mμ we have a *true solution;* if the particles have diameters between 1 mμ and 0.1 μ it is customary to think of the particles as being in *colloidal solution*, and if the particles do not settle out but have diameters larger than 0.1 μ we have what is called a *suspension* although it must be emphasized that this division is arbitrary and there are really no sharp lines between a true solution, a colloidal solution and a suspension.

The physical properties of a true solution (osmotic pressure, lowering of the freezing point, raising of the boiling point, etc.) are determined by the concentration of the solution. A colloidal solution, on the other hand, shows but little depression of the freezing point or rise in boiling point as compared with the pure solvent.

Two types of colloids are formed from aqueous solutions. Some, like silver chloride, show little, if any, attraction for water. Before coagulation their colloidal solutions are only slightly viscous, and when flocculated, the particles settle in a state easy to filter. Such colloids are called *suspensoids* or *hydrophobic* colloids. The colloid held in suspension is called a *sol.* Most of the difficultly soluble inorganic precipitates will yield sols of the above type. The second type of colloid has a marked affinity for water; in the dispersed state (or sol form) such colloids have high viscosity, and when coagulated they settle out in the form of gelatinous solids (*gels*) which retain large quantities of water in a dispersed condition. This type of colloid is called an *emulsoid* or *hydrophylic colloid.* Silicic acid and hydrated alumina are familiar examples of this type. The distinction between these two kinds of colloids is not an absolute one. In the dispersed state, both types form *sols* or *hydrosols* if the dispersion medium is water. From the hygroscopic gels it is hard to remove all the water, even by strong ignition, but the suspensoids form precipitates which are easy to dry.

It was formerly customary to classify solids as either *crystalline* or *amorphous*, and when this distinction was made it was thought that *true* solutions were obtained from crystalline substances and *colloidal* or pseudo solutions were formed from amorphous solids. This distinction does not seem to be fundamental because many apparently amorphous substances have been found to consist of extremely small crystals and some liquids possess crystalline properties. The size of the particles, as stated above, seems to be the more important criterion. Crystalline solids are characterized by a definite shape of the individual particles. The sides are plane surfaces, and the angles they form with one another are characteristic and always the same for a given crystal. When a beam of X-rays is passed through crystalline material, there is obtained a diffraction pattern of X-rays scattered at various angles from the direction of the beam. From such X-ray studies, it has been shown that the essential feature in a crystal is the arrangement of the atoms, ions, or molecules in a definite pattern which is repeated throughout the crystal. Each positively charged atom is surrounded by a number of negatively charged ones, and conversely for each negatively charged particle. These tiny particles, definitely separated from one another, form what is called the *lattice* of the crystal. The spaces between these particles sometimes permit other material to be entrapped.

Flocculation and Peptization. Colloidal solutions are to be avoided in analytical chemistry because the colloidal particles are so small that they cannot be removed by ordinary filtration. The small particles will remain in a dispersed condition as long as their kinetic motion is sufficient to overcome the gravitational attraction which tends to cause sedimentation. The dispersed particles can be kept in suspension by acquiring an electric charge. This is accomplished by the adsorption of anions or cations on the surface of the particles. Thus metal sulfide sols adsorb sulfide ions, and these are attracted so strongly that they are fixed on the surface of the particles. Whenever such adsorption takes place, there must be adsorption of some oppositely charged ion to preserve neutrality. If a sulfide precipitate adsorbs negatively charged sulfide from hydrogen sulfide, the hydrogen ions cannot approach the surface so closely and will remain a slight distance away, since the electrostatic forces between the negative ions on the surface and the positive *counter ions* (in this case hydrogen ions) are large. A so-called *electrical double layer* is set up between the particles and the solution, the existence of which is responsible for the stability of the sol. All the particles of the sol have the same electric charge and cannot, therefore, approach one another closely. If the double layer is destroyed, as by the addition of a suitable electrolyte, floccuation results. The minimum quantity of electrolyte necessary to flocculate a given colloid is called the *flocculation value*, and it varies with different electrolytes. Thus, to flocculate negatively charged arsenic trisulfide sol, 1000 times as much NH_4Cl is required as $AlCl_3$.

When a colloidal precipitate is washed with pure water, some of the adsorbed ions may be removed, and if the concentration of this ion in the wash water is below the flocculation value, the particles of the precipitate are likely to go back to the sol condition. This is called *peptization;* it can be prevented by washing the precipitate with a suitable electrolyte, preferably one which can be subsequently removed by heating.

Sometimes the absorptive power of a precipitate can be used to advantage; for example, hydrated stannic oxide will adsorb H_3PO_4 and H_3AsO_4 and remove them completely, provided that sufficient colloid is present.

Precipitates formed from very dilute or from very concentrated solutions are in the form of extremely fine crystals with colloidal properties. Thus unfiltrable precipitates of barium sulfate are obtained from solutions which are above 0.75 N in concentration or less than 0.001 N. The precipitates are composed of such tiny crystals that they appear to be amorphous.

Aging of Precipitates. Very fine precipitates often become filtrable if allowed to stand for some time in contact with the mother liquor. Keeping the solution near the boiling point often helps to flocculate a precipitate, and the addition of some macerated filter paper pulp is helpful in filtering colloidal material. The crystals that first form are likely to be imperfect; on standing they tend to perfect themselves. Small particles have a slightly greater solubility than the larger particles; after standing the smaller crystals disappear and the others grow larger. Sometimes the precipitate that forms first is a metastable modification which, on standing, is changed to a more stable and less soluble state.

Coprecipitation. Precipitates are seldom perfectly pure. They may contain a little mother liquor or substances which are normally soluble under the prevailing conditions. Thus, when barium sulfate is formed by adding barium chloride to a solution of potassium sulfate, the precipitate contains a little potassium which is hard to remove by washing, although potassium sulfate is easily dissolved by water. We say that potassium sulfate is *coprecipitated.* This coprecipitation is often caused by adsorption on the surface of the crystal. Adsorption during the growth of a crystal is called *occlusion;* it is different from *inclusion,* which occurs when some mother liquor is entrapped. Sometimes a *solid solution* (also called *mixed crystals*) is formed of two substances which have the same crystalline characteristics. Thus $PbSO_4$ sometimes crystallizes with $BaSO_4$ to form a homogeneous mass or "single phase."

Postprecipitation. Many precipitates are deposited slowly and the solution remains in a state of supersaturation for a long time. Thus, when calcium oxalate is formed in the presence of considerable magnesium ions, the precipitate of $CaC_2O_4 \cdot H_2O$ is practically pure at first, but when it has stood for some time, gradually some of the magnesium is precipitated. Similarly with sulfides, we find that zinc sulfide, for example, is precipitated more readily when a precipitate of HgS or CuS is present. Since, by the precipitation of CuS or HgS from a solution, the acidity of the solution is increased as shown by the equation

$$Cu^{++} + H_2S \rightarrow \mathbf{CuS} + 2H^+$$

one might expect that ZnS would form more readily from, say, a solution which is 0.1 N in HCl, in the absence of copper ions, although the reverse is true. The coprecipitation of the zinc with copper can be explained by the fact that the copper sulfide precipitate has strong adsorptive powers toward H_2S and, as a result, the concentration of H_2S is greater at the surface of the precipitate than at other parts of the solution.

Filtration and Washing of Precipitates

How large should the filter be, and how many times should the precipitate be washed?

With regard to the second question it is evident that the precipitate should be washed until the soluble, non-volatile matter is completely removed. It is clear, however, that this point will never be reached because a part of the solution always remains on the filter, but it is not difficult to make the amount of the dissolved substance remaining so small as to be negligible. When the amount of dissolved substance remaining on the filter is so small that it could not be detected by the balance, the precipitate can be considered to be completely washed.

The aim should be not only to remove the soluble matter, but also to accomplish this with as little wash water as possible.

No precipitate is absolutely insoluble, so that it is clear that every unnecessary excess of wash water causes harm by removing a fraction of the precipitate, and the greater the excess of the wash water the greater the amount of the precipitate dissolved.

The amount of wash water to be used depends largely upon the nature of the precipitate itself. Amorphous, gelatinous precipitates always require more washing than crystalline, granular ones. As a rule, it may be said that the process of washing must be continued until the substance which is being washed out can no longer be detected in the last filtrate. If the filtrate must be used for another determination, it is obvious that it should not be tested too soon.

Let us assume the filter to hold 10 ml, the solution to drain to the last drop from the paper, the amount of the solution held back by the precipitate and filter to be 1 ml and to contain 0.1 g of the solid substance which is to be removed by washing.

The filter is filled to the upper edge with wash water and allowed to drain to the last drop n times, until not more than 1/100 mg of the substance to be removed by washing remains.

According to our assumption, 9 ml drains off and 1 ml remains behind; consequently we have:

Removed by the		There remains after the	
1st washing,	$0.1\cdot\frac{9}{10}$ g	1st washing,	$0.1\cdot\frac{1}{10}$ g
2d "	$0.1\cdot\frac{9}{10}\cdot\frac{1}{10}$ g	2d "	$0.1\cdot\frac{1}{10}\cdot\frac{1}{10}$ g
3d "	$0.1\cdot\frac{9}{10}\cdot(\frac{1}{10})^2$ g	3d "	$0.1\cdot\frac{1}{10}\cdot(\frac{1}{10})^2$ g
.		.	
.		.	
.		.	
nth "	$0.1\cdot\frac{9}{10}\cdot(\frac{1}{10})^{n-1}$ g	nth "	$0.1\cdot\frac{1}{10}\cdot(\frac{1}{10})^{n-1}$ g

After n washings, therefore, the amount removed by washing is the sum of the decreasing geometric series of which the first term is $0.1 \cdot \frac{9}{10}$ and the constant factor is $\frac{1}{10}$.

If $n = 4$, the sum of the series is

$$\Sigma = \frac{0.1 \cdot \frac{9}{10}\left[\left(\frac{1}{10}\right)^4 - 1\right]}{\frac{1}{10} - 1} = 0.09999 \text{ g}$$

After four washings of the precipitate, therefore, 0.09999 g of the impurity has been removed. According to the assumption that there was originally 0.1 g of this substance, there remains in the precipitate only 0.00001 g, or in other words a negligible amount.

Consequently, the filtrate should be tested qualitatively for the substance to be removed only after the precipitate has been washed four times.

Often the washing will be found to have been complete after the fourth washing, but as a rule this will not be so, and in many cases it will be found necessary to repeat the operation for ten to twenty times. In the processes which are described it will usually be stated how far to carry the washing.

Now in order to wash a precipitate with the least possible amount of wash water, it is evident that the size of the filter paper will have an effect. The filter should be made as small as possible, irrespective of whether there is little or much liquid to filter. *The size of the filter used should be regulated entirely by the amount of the precipitate and not at all by the amount of the liquid to be filtered.* The mistake should not be made, however, of using too small a filter. The precipitate should never reach the upper edge of the paper; about 5 mm should remain free, and even then the filter should not be so completely filled as in Fig. 15*a*. It is better to have the filter filled about as much as is shown in Fig. 15*b*, in order that sufficient room is left for the wash water.

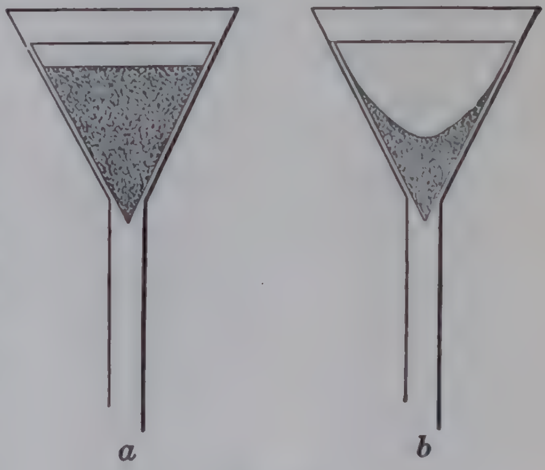

Fig. 15.

The use of too large filters is one of the inexcusable analytical errors.

Equipment and Manipulation

Paper Filters. Strength, uniform texture, proper porosity, and a low ash are the desirable qualities in filter paper for quantitative work. A paper of 7-cm diameter should have an ash of less than 0.05 mg. To get this low ash, the paper has been washed with hydrochloric and hydrofluoric acids. This washing makes the paper softer and more porous but weakens it so that it is more easily torn.

The purpose of filtration is to separate a solid from the liquid in which it is suspended. The pores of the paper must be smaller than the particles of solid which are to be retained by the filter. Precipitates vary with respect to the size of the smallest particles. Some, like crystalline barium sulfate or gelatinous metastannic acid, are very finely divided and require a fine-grained paper. Such filter paper is a slow filtering medium. Consequently chemists are accustomed to use different grades of filter paper, some which make rapid filters and others which make slow filters but are required for precipitates that are likely to pass through the pores of a rapid filter paper.

Funnels are supposed to have an angle of exactly 60°, and the simplest way to fold a circular cut paper is to crease it across a diameter and then, without opening the paper, make a second fold at right angles to the first one. To test the funnel, and this should always be done before starting to filter, open the filter so that it makes a cone to fit the funnel, wet the paper, and see if it fits tightly against the side walls of the funnel. It is important that it should fit tightly along the upper edge, which must always be below the rim of the funnel as otherwise the filter cannot be washed satisfactorily. Pour water into the funnel, and if the filter fits, the stem should fill with liquid. If the stem is too wide, this will not always happen. A little grease in the stem of the funnel will also interfere. If the filter does not fit when folded into a 60° cone, change the second fold sufficiently to make it fit.

It is convenient to mark the funnel so that it can always be told how much the second fold should be changed to make the filter paper fit the funnel. It is also well to mark the funnel so that it can be recognized as a rapid or as a slow funnel, for funnels vary greatly in this respect.

The above method of folding a filter paper is the easiest and quickest, but often considerable time is saved in the filtration by folding the paper so that liquid passes through it more rapidly. The following method of folding a filter accomplishes this end, but it is harder to make the filter fit tightly to the funnel and there is more danger of having a little precipitate get by the filter.

1. Fold the paper evenly across a diameter of the circle as in the above method.

2. Open up the fold and make another at right angles to it creasing the paper on the same side as at first. This is done by merely bringing

the two points on the circumference of the circle that were met by the first fold over against one another and flattening out the paper again.

3. Turn the paper over and fold again exactly 22½° away from one of the first two folds. To get this position, bisect one of the quadrants formed by the previous two folds, by merely bringing two creases together and flattening out the paper so that a little crease is made on the circumference, and make another bisection in the same way. At this last mark fold across the paper with the crease on the opposite side to that made by the original folds.

4. Open up the paper and make another fold at right angles to the third fold. Change half of this last fold to make the paper fit the funnel.

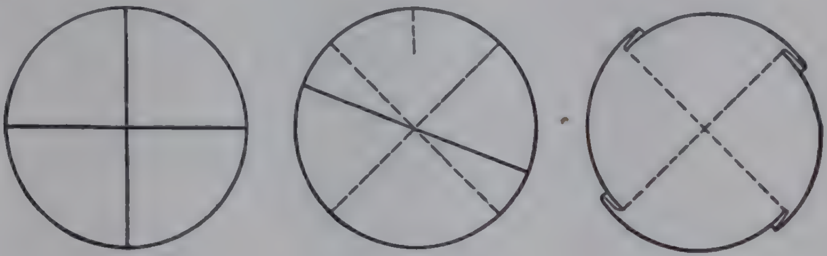

FIG. 16.

Figure 16 shows three stages in folding a filter by the method just described, which has been called *the quadruplet method* because four folds are made instead of the usual two.[1]

For large funnels a *plaited or fluted filter* is often desirable. These can be purchased already folded, but the quality of the paper is not always suitable for quantitative work. Swedish filter paper is satisfactory for most purposes when the filter itself is not to be ignited. This can be purchased in sheets, and one-quarter sheet is sufficient for a large funnel. Since all filter paper retains some of the solution poured through it so firmly that it is very difficult to remove the last traces of solute by washing, it is never wise to choose a large funnel simply because considerable liquid has to be filtered. To make a plaited filter:

1. Fold the filter once along a diameter as in the first method. Do not open this fold.

2. Make a second fold along the radius as in the first method.

3. Open this second fold and make two other folds at right angles to each other, dividing the doubled filter into quarters. This is accomplished by taking half of the straight edge of the once-folded filter and folding it over to make it coincide with the second fold. Take care

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[1] Mellon, *Methods of Quantitative Analysis.*

to make all these folds accurately, but do not crease the paper hard at the center.

4. With the paper again folded only once, make a fold dividing one of the outside segments into halves and make a fold at right angles to this by bringing over the other half of the straight edge.

5. Make two more folds starting with the other outside segment.

By these seven folds the original circle is divided into sixteen parts of equal size, and if the paper is opened, half of the creases will be found all on the same side in one half of the paper and all on the other side in the other half of the paper.

6. With the paper again doubled as it was after the first fold, start at the outside, fold over into the first crease and then bring back the outer edge so that it is in line with the outer edge of the first crease. This makes a subdivision of the outside segment and brings the crease on the opposite side of the doubled paper.

Without opening this last fold, go into the next crease and again come back continuing until the middle fold is reached.

Start in the same way at the other side of the doubled paper and plait toward the center as from the other side.

In this way the paper will be divided into thirty-two equal segments. If the filter is made from a quarter sheet of Swedish paper, it is not necessary to cut out a circle at the start. When the plaiting is finished it is easy to tear off the ends of the folded paper so that it will fit into the funnel, without protruding above the edge, and leave a nearly circular edge.

Plaited filters are used chiefly when it is desired to filter off a large and bulky precipitate and it is not necessary to wash the precipitate thoroughly. Plaited filters made from Swedish paper filter rapidly but are likely to break at the point of the cone.

It is rarely advisable to use suction with a paper filter. The suction is likely to draw small particles of the precipitate into the pores of the paper and then filtration is usually as slow as or slower than it would have been without the suction. If suction is used with a paper filter, the filter should rest in a filtering cone made of platinum, palau, or a hardened parchment filter.

Stirring Rods. Each student should have six or eight stirring rods of suitable lengths. The rod when resting in a beaker should project about 3 cm beyond the lip of the beaker. If small tubing is used, both ends should be sealed; solid rods should be fire-polished at each end. At least one rod should be fitted with a rubber tip (policeman) for removing precipitates which adhere to the walls of beakers. The use of the stirring rod in filtering a solution is shown in Fig. 17. The way the stirring rod is used in transferring a precipitate to a filter by means of a jet of water from a wash bottle is shown in Fig. 18. Note in both illustrations that the end of the funnel stem is close to the side of the beaker. The funnel should never be allowed to dip into the filtrate, and when it empties into the middle of the beaker there is more or less spattering.

Filtering Crucibles. The use of a filtering crucible with perforated bottom was first suggested by F. A. Gooch.[1] The preparation of asbestos fibers as a filtering medium and the use of the Gooch crucible were described in connection with the filtering of a permanganate solution on p. 110. If the Gooch crucible and the asbestos are heated to the temperature at which it is desired to heat the precipitate, cooled in a desiccator, and weighed, then the gain in weight after the precipitate has been transferred to the crucible, washed, and heated, represents the weight of the precipitate.

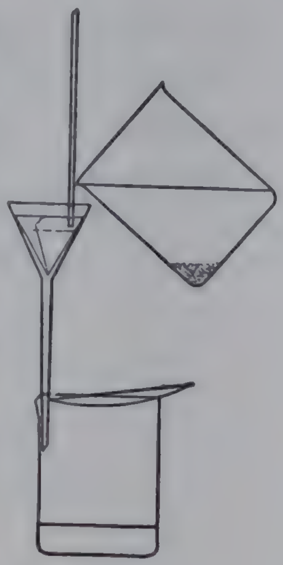

FIG. 17.

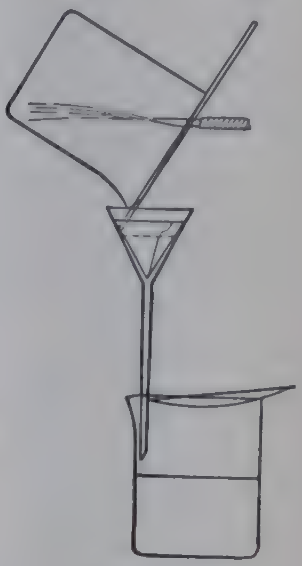

FIG. 18.

Often it is sufficient to heat the product to a temperature of 105°, for which purpose an automatically controlled electric oven is very serviceable. If it is desired to heat the precipitate to a higher temperature, the Gooch crucible should be heated inside another crucible or in an air-bath so that the gas flame does not play directly against the holes in the crucible. Electric ovens are also made which permit drying at temperatures up to 1000°.

The so-called Munroe crucible,[2] in which the filtering medium consists of a porous felt of spongy platinum, is a modification of the Gooch crucible which permits rapid and accurate work. The felt is prepared by igniting a carefully dried layer of ammonium chloroplatinate, which has been poured over the bottom of a platinum Gooch crucible in the form of an alcoholic sludge while the crucible is held against several layers of filter paper. The felt can be shaped to the crucible during the ignition and subsequently burnished lightly with a glass rod of suitable form. If imperfections develop, the felt should be saturated again with chloroplatinic acid, the crucible slowly lowered into a moderately concentrated solution of ammonium chloride, washed with alcohol, dried, and ignited. On account of the high price of platinum, the present tendency is to avoid its use as much as possible so that the Munroe crucible has never been popular. The Norton Company of Worchester, Massachusetts, make *Alundum* filtering crucibles which are very rapid but are rather slow to dry to constant weight at low temperatures. Filtering crucibles are also made with sintered-glass porous bottoms with different degrees of porosity; they can replace the Gooch crucible to advantage for most purposes.

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[1] *Proc. Am. Acad.*, **13**, 342 (1878); *Am. Chem. J.*, **1**, 317.

[2] C. E. Munroe, *J. Anal. Chem.*, **2**, 241; *Chem. News*, **58**, 101. See also W. O. Snelling, *J. Am. Chem. Soc.*, **31**, 456, and O. D. Swett, *ibid.*, **31**, 928. The last reference gives a table of suitable solvents for removing ignited precipitates from the Munroe crucible.

Triangles. For use with platinum crucibles, platinum triangles are desir-

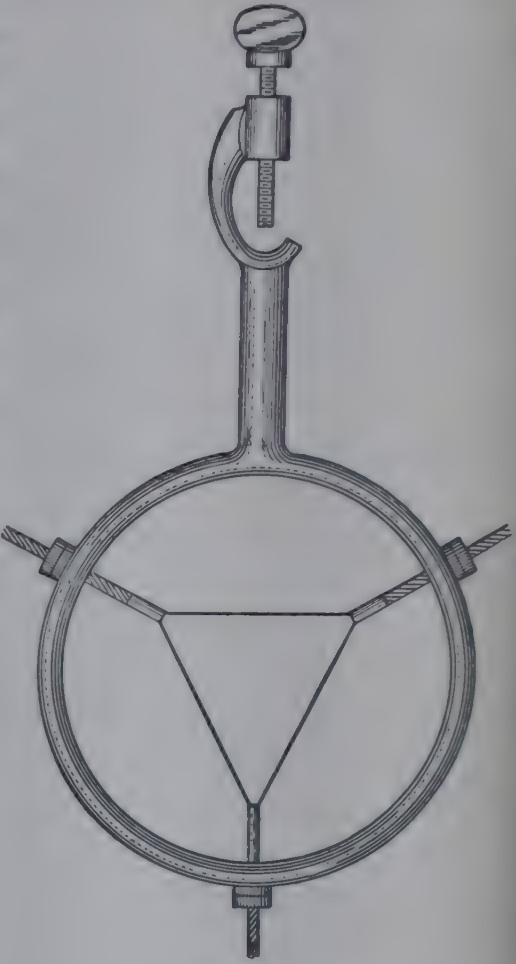

FIG. 20.

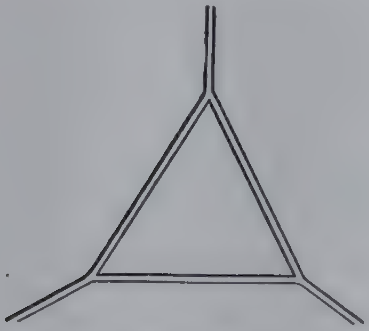

FIG. 19.

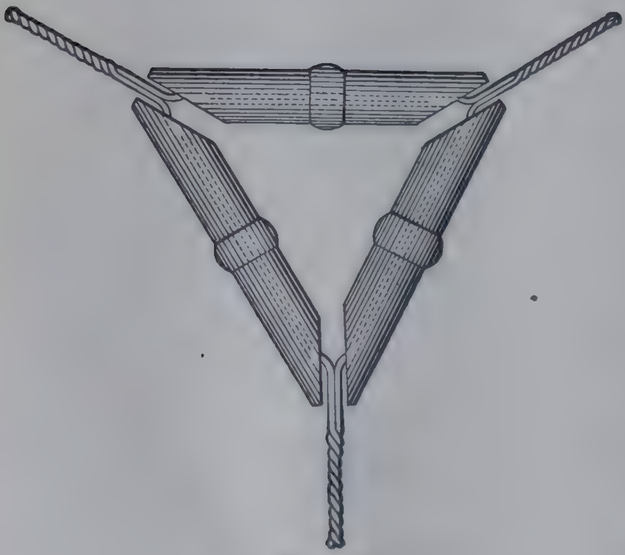

FIG. 21.

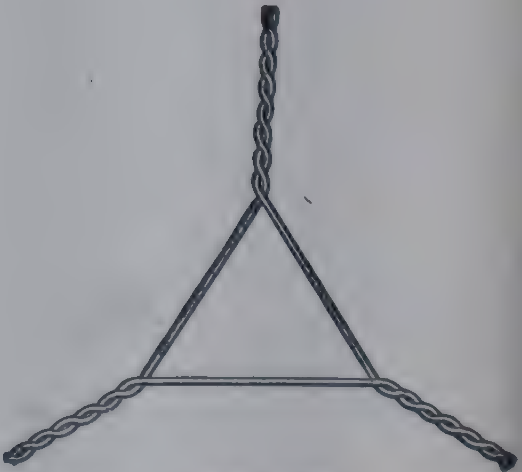

FIG. 22.

able. Figures 19 and 20 represent two forms of these. The first is made of heavy platinum wire and is intended to rest on the ring of a lampstand. The second form is made so that it can be screwed on to the ring and thus kept in place.

Figure 21 shows a clay triangle which can be used even for platinum crucibles, and Fig. 22 represents a less expensive nichrome triangle. This may be used with platinum if it is kept clean and no flux is spilled upon it, but there is some danger of staining the crucible with this kind of a triangle.

Triangles of fused quartz are also useful. Figure 23 shows the correct and incorrect ways of placing a crucible on a triangle in an inclined position.

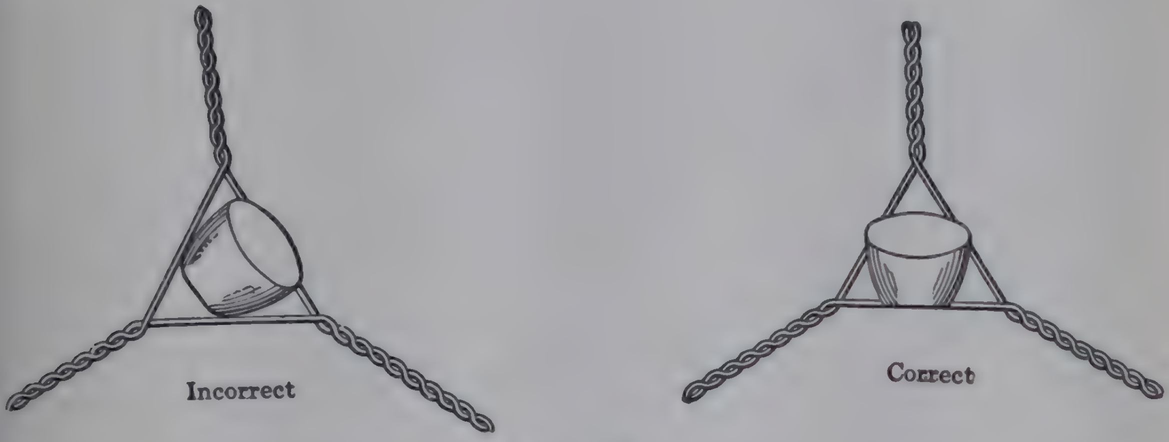

Fig. 23.

Burners. Besides the ordinary Bunsen burners which are familiar to all, two other types deserve mention. The Tirrill burner is based upon the principle of the Bunsen burner but is an improvement in design. At the base of the burner the flow of gas is regulated by a screw which operates a needle valve, and the supply of air is regulated by screwing the tube of the burner up or down and thus allowing more or less air to enter through the holes at the base.

The Méker burner provides for a similar adjustment of gas and of air but the shape of the burner tube is different. The tube is narrowest near the base and widens out at the top. As a result the delivery of the gas under pressure into the inverted cone causes a greater reduction of pressure within the tube and a greater inflow of air than in other burners which do not operate with a blast. There is a more perfect mixing of the gas with air and a greater combustion of gas within a given space. At the top of the burner tube is fitted a nickel grid, and the gas burns in a great many small flames with the tip of each inner reducing cone about 1 mm above the top of the burner. The many small flames unite to give a very hot and highly concentrated flame which is oxidizing in character except below the tips of the tiny flame cones. A crucible placed just a little above these tiny flames is heated nearly as hot as by a blast lamp.

Distilled Water. Various forms of stills are in common use. It is important that the vessel containing the boiling water should be so separated from the condenser that there is little danger of spray entering it. The boiler may be of any material, but the condensing worm and supply pipes should be of pure tin.

Distillation does not free water from carbon dioxide, oxygen, nitrogen, and ammonia, and supply tanks are likely to become slimy after a time. For water analysis and in any work involving the use of water free from nitrogenous compounds, it is necessary to distil the water a second time with permanganate in the boiler. The first and last runnings are then rejected.

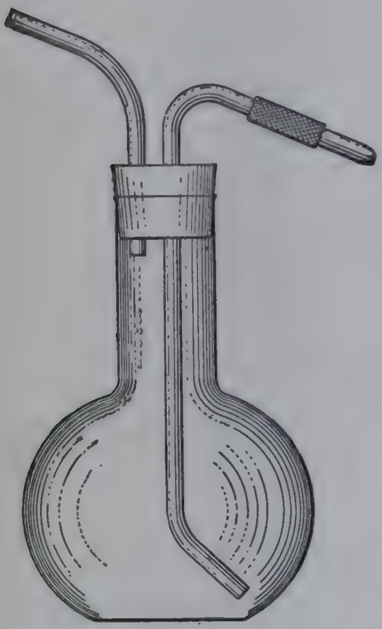

FIG. 24.

Wash Bottles. For transferring a precipitate to a filter and for washing it, a *wash bottle* is indispensable. Figure 24 shows a sketch of the type most commonly used. It consists of a flat-bottomed, 750-ml flask fitted with a rubber stopper and glass tubing bent so that the mouth-piece and outlet tubing are in line. It is best to make the outlet tube in two pieces so that the jet can be manipulated by moving two fingers of the same hand that holds the bottle. The nozzle may be made by drawing out tubing until a capillary is formed and then cutting off to make a stream of the proper size. A stouter tip may be made by simply fusing the end of the original tubing until it has contracted to the proper diameter.

The bend of the long piece of tubing inside the flask is made so that this reaches into the deepest part of liquid when the wash bottle is inclined slightly as in washing precipitates. A bend of the opposite kind is useful for washing precipitates out from beakers, when the bottle is inclined in the opposite direction.

In washing the filter, the stream should always be directed against the upper edge of the paper; this is the hardest part of the paper to wash.

For washing with organic solvents that dissolve rubber, a bottle with a ground-glass stopper is desirable but it is unnecessary for most work in inorganic chemistry.

The wash bottle shown in Fig. 25 is useful for work with hot water or with bad-smelling wash liquids. It contains two tubes like the ordinary wash bottle but at the end of the tube A a Bunsen valve is placed. This is made by cutting a slit in a short piece of rubber tubing, placing this on the end of the tube through which one blows in using the bottle, and sealing the other end of the rubber tubing with a piece of glass rod. On blowing, the slit opens but closes to prevent escape of steam. The third tube C is closed by the finger when using the bottle or by means of rubber tubing and a pinchcock. After blowing through A, a stream of water is ejected at B if C is kept closed. When C is opened the stream stops. It is well to wind the neck of the wash bottle with heavy curtain cord, if it is to be used for hot water.

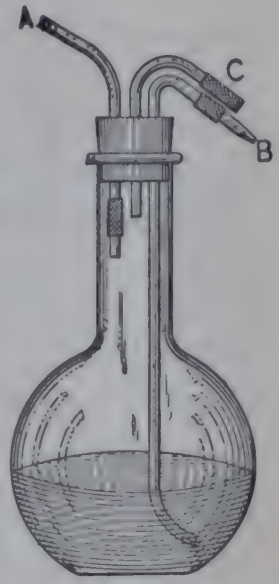

FIG. 25.

Policemen. Sometimes a little precipitate adheres to the side of a vessel. To remove it, a piece of rubber over the end of a glass stirring rod is used. This so-called *policeman* may be made by sticking together the end of a piece of rubber tubing that fits the rod tightly, or it may be purchased from a chemical supply house. The policeman should not as a rule be used for stirring a solution and should not be allowed to remain in solutions.

Transfer of Liquids. In pouring out a reagent from a bottle never place the stopper on the work-bench. Pick up the stopper between the first two fingers of the right hand with the palm up, grasp the bottle with the same hand and the palm over the label, and pour from the bottle with the label up so that there is no danger of any liquid falling upon the label. It is advisable to cover printed labels with thin coatings of gum sandarac dissolved in alcohol. In pouring liquids it is always advisable to pour against a glass rod so that none of the liquid is spilled. In removing the rod do not move it upward and scrape off a little liquid thereby. It is well to give the rod a slight downward motion on taking it away.

Reagents and Glassware. One of the greatest sources of trouble for the analytical chemist is the presence of impurities in reagents and the action of solutions upon glassware. It is desirable to buy the purest possible reagents, but the chemist should always take care to test them. Even if the reagents are perfectly pure, they often become contaminated by solutions remaining in glass bottles. In every analysis, therefore, errors are likely to arise from impurities that were in the reagents or from glassware that has been somewhat dissolved. Solutions of strong acids and bases when kept for some time in bottles will always give a slight test for silica if sufficient reagent is taken for the test.

Today it is possible to buy glassware which is much less acted upon by reagents than that formerly used. Such glass is essentially a borosilicate of sodium, zinc, and aluminum.

It is well sometimes to run through blank analyses to see whether any weighable precipitates are obtained when the reagents alone are used in an analysis. Such analyses are often misleading because the precipitates are so small that they may be overlooked or they may be so fine that they need some other precipitate to absorb them and prevent their passage through the filter.

The Evaporation of Liquids. Liquids are usually evaporated upon the water bath. In order to prevent anything from falling into the solution, the beaker or dish should be covered with a watch glass which is raised sufficiently by a glass triangle, or a " watch-glass support " to permit escape of the volatilized solvent. Under no circumstances, should the solution be boiled during evaporation as a little of the solution is always carried up with the escaping vapor from a boiling solution.

The Drying and Igniting of Precipitates. Before a precipitate can be weighed it is usually necessary to dry it. Those precipitates which do not undergo a change of weight on ignition are treated as follows:

(*a*) *The Precipitate Is Ignited Dry.* This method, in which the precipitate is separated from the filter, the filter burnt by itself, the ash added to the main part of the precipitate, and the mixture then ignited to constant weight, is used when the ignited substance will be reduced by the burning paper, for example, precipitates of silver chloride, lead sulfate, bismuth oxide, etc.

To perform this operation it is first desirable to dry the filter and precipitate at 100°. Wet a common filter, stretch it over the top of the funnel, and then gently tear off the superfluous paper. The cover thus formed continues to adhere after drying. Place the funnel and filter in a drying-closet and dry at 100–105°. When they are perfectly dry, place a weighed crucible upon a piece of glazed paper of about 20 sq cm (Fig. 27, left) and carefully shake the dry precipitate into the crucible, removing it from the paper as completely as possible by gentle rubbing with a platinum spatula. Brush into the crucible with the aid of a feather any small particles of the precipitate which may have fallen upon the glazed paper (Fig. 27). Small particles of the precipitate will still always adhere to the paper, and these must be weighed. In order to accomplish this, set fire to the filter and weigh the ash by itself or mixed with the main part of the precipitate.[1]

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[1] By using filter paper which has been carefully washed with hydrochloric and hydrofluoric acids, it is permissible to neglect the weight of the ash from the filter

The combustion of the filter, to which small particles of the precipitate still adhere, is best accomplished by the method proposed by Bunsen as follows: Fold the filter together so that the precipitate occupies the position indicated in the shaded part of Fig. 26 α, and then fold again as indicated by β and γ of Fig. 26 to a narrow strip. Roll up the paper as indicated by δ, beginning at b, so that the portion of the filter which is free from the precipitate is on the outside. Place the roll in the loop of a platinum wire, hold it over the crucible (see Fig. 27), and set fire to the filter by means of the gas flame. Take away the flame and allow the paper to burn quietly. If carbonized particles still remain, apply the gas flame repeatedly until it is no longer possible to make the particles glow any more. (Too strong ignition should be avoided.) Add the ash to the contents of the crucible by gentle shaking and the final use of the feather. Heat the crucible at first with a small flame, and gradually raise the temperature until the prescribed temperature of igni-

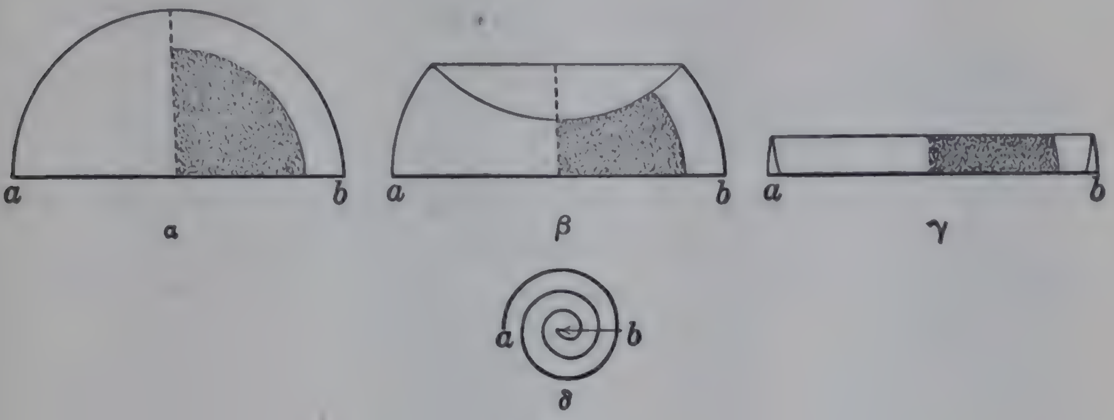

FIG. 26.

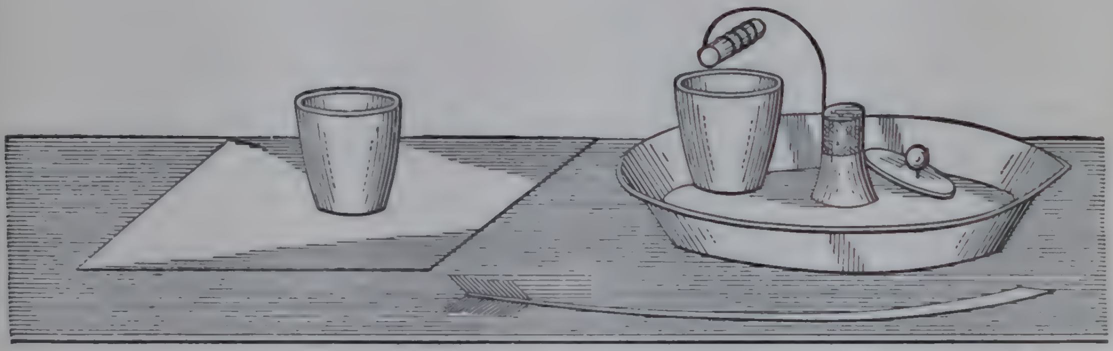

FIG. 27.

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itself. With an unknown paper it is necessary to determine the weight of the ash by a separate experiment and then correct the weight of the precipitate obtained.

tion for the given precipitate is reached. Finally remove the flame, allow the crucible to cool somewhat, and while still it is *warm*, but *not glowing*, place it in a desiccator (Fig. 28).

After cooling (at least three-quarters of an hour for porcelain crucibles and 20 minutes for platinum ones) weigh the crucible and its contents.

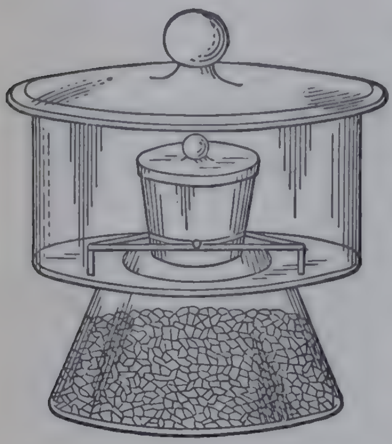

FIG. 28.

Many precipitates (silver chloride, lead sulfate, etc.) are partially reduced to metal by the above treatment. As these metals are difficultly volatile, however, there will be no loss of the metal, only of the anion (chlorine in the case of silver chloride and SO_4 in the case of lead sulfate). This loss may be readily replaced. Moisten the metal in the crucible with a few drops of nitric acid to dissolve it, add a few drops of hydrochloric acid (in the case of a silver chloride precipitate), or of sulfuric acid (in the case of lead sulfate), and after evaporating off the excess of the acid, weigh the crucible. The only danger in this method is that in burning the filter the ash is heated too hot, so that some of the reduced metal melts and alloys with the platinum wire. If, however, the filter paper is rolled up as was directed, there is always some paper free from precipitate between the precipitate and the platinum wire, yielding an ash which, although its weight is inappreciable, is still sufficient to protect the wire and prevent the reduced metal from coming in contact with it, provided that it is not heated strongly enough to melt the metal.

Many precipitates (K_2PtCl_6, etc.) are changed so much by this treatment that it would be impossible to obtain correct results. With such precipitates the filter cannot be burnt, but it is previously dried at a definite temperature and weighed; afterwards the precipitate and filter are again dried at the same temperature and weighed again.

For drying precipitates an electric oven with automatic temperature control is most advantageous. The regulator can be set at the desired temperature, which will be maintained indefinitely within a few degrees.

(*b*) *The Precipitate Is Ignited Wet.* Those precipitates which do not suffer any permanent change by the action of the products of combustion of the filter may be ignited wet. Allow the precipitate to drain as much as possible, and while still moist place the filter and precipitate in a crucible, with the paper folded so that the precipitate is not exposed and so that the moisture will be expelled through a layer of paper and not directly into the air. Place the crucible in an inclined position upon a triangle (Fig. 29),[1] with the cover inclined against the upper edge of the crucible and resting on the triangle. Direct the flame of the burner against the cover, which quickly dries the filter, then scorches it. Before it takes fire, move the flame to the back of the crucible and heat with a small flame until all the paper is consumed without taking fire, then slowly increase the temperature until finally the crucible is subjected to the whole heat of the burner, after which it can be heated over the blast lamp if necessary.

Always in igniting precipitates care should be taken to raise the temperature slowly. The object in keeping the flame near the mouth of the crucible at the start is to make sure that the contents of the crucible are dried from the outside. If the flames were placed at the base of the crucible at the start, there would be more danger of loss by spattering. It is better to use a small flame near the crucible than a large flame with the crucible raised. Care should be taken not to let the paper take fire, except when the bulk of the precipitate has been removed from it and is ignited separately. When the paper burns rapidly in the crucible there is danger of a slight mechanical loss due to the rapid escape of the products of combustion.

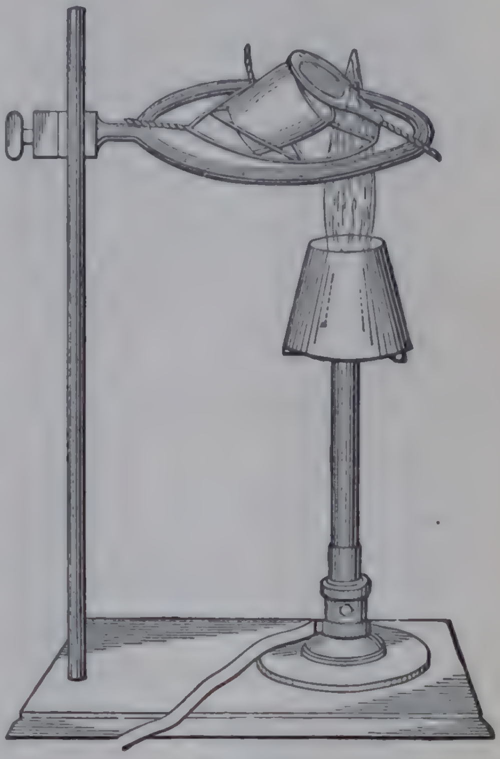

FIG. 29.

Too rapid heating of a paper filter may cause two other errors. Often the temperature is raised rapidly enough to fuse a little salt around the ash of the paper, and carbon inside such a fused coating is hard to burn because it is out of contact with the air. This is true, for example, of a silica precipitate, which is likely to retain a little adsorbed alkali salt. If the precipitate is heated rapidly a little carbon is likely to remain even after long ignition over the blast lamp.

Another serious error is sometimes caused by an undesirable reduction. If the filter paper is smoked off slowly at a low temperature it is possible to heat magnesium ammonium phosphate in a platinum crucible without damage to the crucible or to heat ferric hydroxide without getting any magnetite formed.

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[1] In Fig. 29, the inner triangle is platinum wire, the outer triangle is heavy iron wire. Triangles of fused silica or of nickel-chromium alloy are suitable (cf. p. 175), but platinum alloys with iron, so that a hot crucible should never be placed in contact with iron wire.

In the case of magnesium ammonium phosphate it is quite likely that the reduction may be caused by ammonia as well as by carbon. The same principle holds, however, for if the ammonia is expelled slowly at a low temperature there is less danger of a harmful reduction than when the precipitate is decomposed rapidly by strong heating.

When the price of platinum was low, chemists were accustomed to use platinum vessels freely. Thus platinum evaporating dishes, crucibles, filtering cones, spatulas, and heavy platinum wire were used in nearly every chemical laboratory. Since the metal has become more expensive, the chemist is learning how to get along without much of it. Glassware and porcelain are now made of better quality and can be used in chemical work without much contamination. Most ignitions can be made in a porcelain or quartz crucible as well as in platinum. More time is required to cool these crucibles after they have been heated, but the chemist learns to do something else during that time and in the end gets more work done by using a number of porcelain crucibles than he used to do with a few platinum ones.

Alundum[1] represents a refractory form of aluminum oxide. It does not fuse below 2050°. Crucibles can be obtained which are similar to porcelain crucibles, although they are not well glazed. Other Alundum crucibles are made more porous so that they can be used for filtering purposes instead of a Gooch or Munroe crucible. Some of them make very rapid filters, but it is hard to dry them and errors due to adsorption are much more serious than with a platinum or porcelain Gooch crucible.

The Properties and Care of Platinum. Platinum melts at 1770° but does not soften much until this temperature is nearly reached. It resists the action of all common acids except aqua regia and solutions containing chlorine. Long contact with acid ferric chloride solution is also injurious. It forms alloys with easily reducible metals, and platinum crucibles are ruined when such alloys are formed. Long contact with hot carbon injures platinum, some carbide being formed. For this reason a crucible should always be heated with an oxidizing flame; the flame should never show a luminous tip, and the top of the inner cone should be below the bottom of the heated platinum vessel.

Fusion with alkali hydroxides injures platinum, but the metal will stand fusion with alkali carbonate. Compounds of phosphorus are likely to be reduced by hot carbon, and the crucible is ruined when phosphide of platinum is formed.

Iridium has been used to harden platinum but the alloy is less resistant to the action of reagents than pure platinum and the iridium is volatilized appreciably by heating over the blast lamp. Even good platinum ware is likely to become frosted by strong ignition but the surface crystals which cause the frosty appearance should be fine and evenly distributed. A poor platinum alloy will often become covered with a whitish coating and with brown iron oxide stains. In buying platinum it is advisable to get *hammered* rather than *spun* ware, which is more likely to have surface cracks. It is well to specify that no distinct, uneven discoloration should result from heating, that treatment with acid should show no test for iron after heating 2 hours, that the loss on heating at 1100° should not exceed 0.2 mg per hour over a period of 4 hours, and that 5 per cent of rhodium instead of iridium should be present as hardening agent.

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[1] Saunders, *Trans. Am. Electrochem. Soc.*, **19**, 333 (1922).

Handle platinum carefully and avoid bending. Use clean tongs for handling hot crucibles, and do not let the tongs come in contact with melted flux.

To clean, use chromic acid for removing organic matter, hydrochloric or nitric acid singly (never mixed) to remove insoluble carbonates or metal oxides. Fuse with sodium carbonate or borax to remove silica or silicates and with alkali pyrosulfate to remove metals or oxides that resist the action of acids.

Never heat platinum with the inner cone of the Bunsen flame touching the vessel; this will cause brittleness.

Do not heat compounds of lead, tin, bismuth, arsenic, antimony, or zinc in platinum. Do not ignite sulfides in platinum, and avoid heating phosphorus compounds except with great care.

Do not attempt to remove fusions with knives, files, glass rods, or other hard tools. Use rubber-tipped rods or solvents.

Polish dull surfaces with sea sand or very fine Carborundum[1] powder.

Preparation of the Substance for Analysis

It is very difficult to give general rules for the preparation of substances for analysis, for it is necessary to proceed differently in different cases. If it is desired to determine the atomic composition of a substance, it is necessary to choose pure material for the analysis. Although this sounds so simple it is often one of the most difficult conditions to fulfill. Many substances are hygroscopic and absorb moisture from the air, which can be removed by heating the substance or by simply allowing it to stand in a desiccator over calcium chloride, provided that the substance itself undergoes no change by this treatment.

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[1] "Carborundum" is the proprietary name of a special make of silicon carbide which is much used as an abrasive.

Many substances containing water of crystallization cannot even be dried in a desiccator, but must be analyzed air-dry. It is always necessary to determine whether the substance to be analyzed possesses a constant weight.

Many commercial salts are prepared pure and can be analyzed directly; usually, however, they have stood for some time in the air and have been handled somewhat, so that they are not so pure as when freshly prepared. Consequently, if it is desired to test the accuracy of an analytical process, the purity of a commercial sample should never be taken for granted. If the substance is soluble in water it can be purified by recrystallization.

Dissolve 10 or 15 g of the commercial salt in the least possible amount of hot water (it is best to use not quite enough water to dissolve the substance *completely*), and pour the hot solution through a plaited filter contained in a funnel with the stem broken off (Fig. 30). This serves to remove all dust or other insoluble impurity. Catch the filtrate in an evaporating dish and cool it rapidly, while stirring constantly, by placing the dish in a larger one containing cold water.

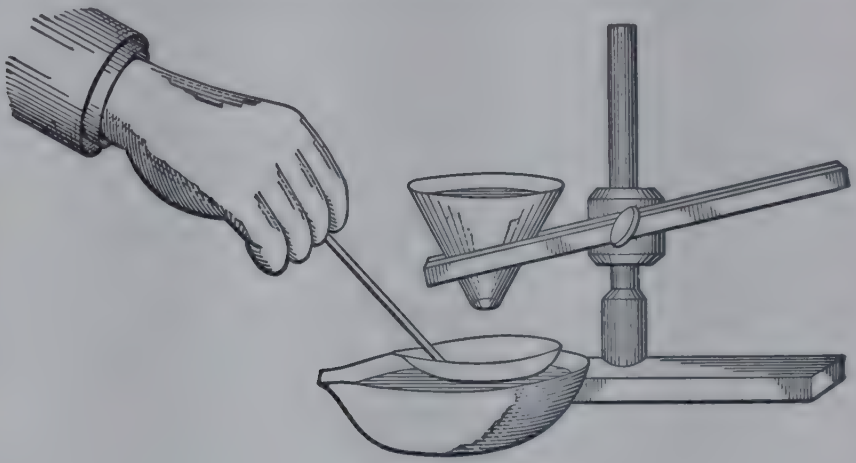

FIG. 30.

By means of the rapid cooling and constant stirring, the salt is obtained in the form of a crystalline powder.[1] Filter off the crystals and drain them by suction. A perforated porcelain plate covered with filter paper may be used in the funnel, or an ordinary filter may be used placed in a perforated filter cone or in a small hardened paper, to prevent tearing the paper by suction. Test the purity of the substance qualitatively by means of some suitable reaction. If it is still not quite pure, repeat the same process of recrystallization until the presence of no impurity can be detected.

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[1] Large crystals would be obtained by allowing the solution to cool slowly, but they are undesirable, as they usually contain more enclosed mother liquor than the smaller crystals. Most water-soluble salts are much more soluble in hot water than in cold water.

Place the pure, moist crystals upon a layer of several thicknesses of clean filter paper, cover with another sheet of filter paper, and allow the crystals to stand for 12 hours at the ordinary temperature. Then weigh out 1 or 2 g of the substance upon a tared watch glass, place it upon a dry glass plate, cover loosely with another watch glass, and allow it to stand for several hours more. If the substance shows no change in weight it is ready for analysis. Otherwise it must be dried in the air until it no longer shows a change in weight. It is permissible to dry in a desiccator only those substances which will not lose water of crystallization. Deliquescent substances, of course, should not be allowed to remain exposed to the air for very long. Such substances must be quickly dried upon a porous plate and transferred as soon as possible to a flask provided with a closely fitting ground-glass stopper.

For *technical analyses*, the purpose being to determine the cost or selling price of an article or to control its manufacture, the substance must be analyzed *as it is*. The sample should represent as far as possible the average composition of the product.

The selection and preparation of representative samples for analysis are matters of so great importance that they have been discussed in more than 1200 papers[1] written since 1892. The quantity of material from which the sample for analysis should be taken varies with the nature of the material. If it is homogeneous it is merely a matter of grinding a portion until it is of suitable fineness.

The Influence of Fine Grinding on Composition

The rate at which a substance dissolves increases as the amount of surface exposed to the solvent is increased, and for this reason solid substances always dissolve more quickly when reduced to a fine powder. Moreover, when a material undergoes chemical attack, an insoluble substance is often formed and, during the process of solution, the insoluble substance may form a protective coating over particles of material that have not been acted upon. This danger is diminished if the material is in the form of a fine powder. For these reasons the chemist usually prefers to grind a solid substance to an impalpable condition before attempting to analyze it.

This practice, though desirable in most cases and absolutely necessary in others, is accompanied by certain disadvantages. If the material is hard there is always some contamination from the material of which the grinding apparatus is constructed. Thus when the sample is ground in a steel mortar or in a steel ball-mill, it will be contaminated with a little iron, and if ground in an agate mortar with a little silica.[1] Again, if the sample readily undergoes slight decomposition, such a chemical change is likely to take place during the operation of grinding. In this way the determination of moisture, of ferrous iron, and of sulfur may be influenced very appreciably.

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[1] Cf. W. J. Sharwood and M. M. Bernewitz, *Bibliography of the Literature on Sampling*, Bureau of Mines Publication. Serial No. 2336.

A number of investigators have pointed out the effect of grinding upon the moisture content of a sample. If the sample is practically dry, it is likely to absorb considerable moisture when dried in the air. Thus Hillebrand[2] found that a piece of unglazed porcelain contained no moisture originally, but showed 0.62 per cent of water when ground. If the substance is very hygroscopic, this danger becomes greater. On the other hand, grinding often causes loss of moisture. This is notably true of substances containing water of crystallization or superficial moisture. Thus grinding can easily reduce the moisture content of a sample of gypsum from 20 to 5 per cent, and a sample of coal may show several per cent of moisture when large lumps of it are tested and very little moisture after it is reduced to a fine powder.

The heat produced by grinding may not only serve to expel moisture from the sample, but it may even cause chemical change. Thus Mauzelius[3] has shown, and the experiment has been repeated by Hillebrand[4] that the ferrous iron content of a rock becomes smaller on account of grinding the rock to a fine powder. It has also been found that some sulfur may be lost by long grinding of a sample of pyrite.

The effect of grinding, therefore, accounts for many divergent results obtained by different chemists who have analyzed the same original material.

Sampling a Shipment

To prepare a representative sample from a large mass of material, such as a shipment of ore or of coal, special precautions are necessary. It is never safe to take samples from the top of a large pile of material, but portions should be selected from all parts. The easiest way to do this is in the loading or unloading of the shipment, taking out portions at regular intervals either by a shovel, trowel, or mechanical sampler. In sampling coal, the United States government[1] takes, as a rule, 1000 pounds from each shipment of 500 tons or less. The size to which ore must be crushed for sampling depends on (1) the weight of material given to the chemist from the shipment,[2] (2) the relative ratio of the richest mineral value and the average value of the ore, (3) the density of the richest material, and (4) the number of particles of the richest mineral. The more " spotty " the ore the larger must be the original weight selected. The results of Brunton's work show that it is necessary to crush the sample before " cutting it down " and advisable after each " cutting " to crush it still finer.

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[1] Hempel (*Z. angew. Chem.*, **1901**, 843) found that an agate mortar and pestle lost 0.052 g in grinding 10 g of glass to a fine powder. E. T. Allen found a loss of 0.145 g of agate in grinding 200 g of quartz.

[2] *The Analysis of Silicate and Carbonate Rocks*, Bull. 700, U. S. Geol. Survey.

[3] *Sveriges Geol. Undersökning*, Årsbok 1 (1907).

[4] *J. Am. Chem. Soc.*, **30**, 1120 (1908).

Crushing the Sample. After enough material has been taken from a shipment to guarantee a representative sample, the next operation is to crush it so that the largest particle is not larger than a certain definite size. Thus, with a sample of coal weighing 1000 pounds, it is all broken up so that the diameter of the largest piece is not more than 1 in. This may be done by a mechanical grinder[3] or by hand with an iron tamping bar or sledge. In mineral analysis, where smaller samples are usually taken, samples are often broken up by pounding on a hardened steel surface with a hardened hammer of the best tool steel.[4]

Mixing and Coning. To mix the sample, it is customary to shovel it into a conical pile. Each shovelful should fall upon the apex of the cone, the material should be thrown so that the cone is not pushed away from its original position, and the shoveler should walk around the cone as he shovels. This serves to bring the finer material near the center of the pile, and the coarser pieces run down the sides. Of the first cone usually one half is rejected. This can be done by shoveling away the cone from the bottom, while walking around the cone, and rejecting every other shovelful. Or the cone may be flattened and quartered.

Quartering. The top of the cone is flattened out and divided into quarters. Opposite quarters are taken for the next crushing.

The mixing, coning, quartering, and crushing should continue until finally a sample of 100–200 g is obtained. When the samples are small enough, the mixing is best done on a sheet of glazed paper, rubber, or oilcloth. A corner of the sheet is lifted and drawn across, low down, in such a way that the material is made to roll over and over and does not merely slide along. The sample should be rolled back and forth along each diagonal for 100 times or more. Then the sample may be spread out into squares and a little taken from each square. In weighing out an ore it is always well to mix it by rolling back and forth unless it is extremely fine, when it is not likely to segregate on standing. Segregation takes place when particles are of different sizes and densities.

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[1] G. S. Pope, *Methods of Sampling Delivered Coal*, Bur. of Mines, Bull. 116.

[2] D. W. Brunton, " The Theory and Practice of Ore Sampling," *Trans. Am. Inst. Min. Eng.*, **25**, 827 (1895).

[3] W. F. Hillebrand, *The Analysis of Silicate and Carbonate Rocks*, U. S. Geol. Survey, Bull. 700.

[4] Mechanical grinders should be made of specially hardened steel and should be built so that they can be kept clean easily. For laboratory grinding, a modified McKenna ore grinder has been recommended by Hillebrand. (*Bull.* 700, U. S. Geol. Survey.)

If, in the sifting of an ore, metallic particles are left on the screen, it is necessary to analyze these particles separately and make a proper allowance in the final calculation. It is necessary then to know the weight of the entire sample and the weight of metal that does not pass through the screen.

In sifting samples, wire screens are commonly used, but inasmuch as a little metal is introduced into the sample, silk bolting cloth is preferable.

The **cutting,** or **dividing,** at the several stages of the sampling process is best done by mechanical means. Some machines, of the riffle type, constantly deflect a part of the material that passes through them. Others, which for some purposes are more desirable, change the direction of the fall of the ore at regular intervals. Buckets are constructed so that, as ore is poured into them, half of it is retained and half rejected. Split shovels, consisting of a series of parallel troughs with equally wide spaces between them, are made of various sizes. The ore retained by the shovel, or that which passes through, may be taken for the sample. In using such shovels, of which the smallest size is useful for weighing out samples that are not perfectly homogeneous, allow a thin stream of ore to fall back and forth over the riffle. The distance between riffles should be at least three times the diameter of the largest particles of ore.

In sampling metals and alloys it is necessary to remember that they are seldom homogeneous. During solidification the part that solidifies last is usually different from that which first separates on cooling. As a rule, the outside of an ingot solidifies first and some of the impurities are likely to be concentrated or segregated in the interior. In a steel rail, microscopic examination often shows that the head, the foot, and the web are not exactly the same. The sample used for analysis should consist of borings taken from all over the rail, or, better still, it should be obtained by planing over the entire cross section. A macroscopic[1] survey of the entire cross section after it has been treated with a suitable etching agent, such as an 8 per cent solution of cupric ammonium chloride or a 6 per cent solution of iodine in alcohol for steel specimens, will often show where segregation has taken place. When metals break under strain, the crack usually starts at some place where the material is defective, usually owing to a little enclosed slag. The analysis of the entire material will often fail to indicate a defective material, and the cause of the fracture can be shown only as a result of metallographic examination of polished specimens under the microscope and the chemical analysis of portions where segregation has been revealed by the microscope.

HOME PROBLEMS

87. If 0.00011 g of AgBr dissolves in 1 l of pure water at 18°, compute the solubility product of AgBr at this temperature. If 6×10^{-7} g of silver arsenate dissolves in 800 ml of water, what is the solubility product of this salt?

88. If the solubility product of $Pb_3(PO_4)_2$ is 1.5×10^{-32}, how many milligrams of the salt will dissolve in 1500 ml of water?

89. From the solubility product of CdS (3.6×10^{-29}) and the facts that the primary ionization constant for H_2S is 0.91×10^{-7}, the secondary ionization constant is 1.2×10^{-15}, and the saturated solution is approximately 0.1 *N* H_2S at 20°, compute the weight of cadmium as CdS (*a*) dissolved by 1 l of pure water, (*b*) by 1 l of 0.3 *N* HCl (completely ionized).

Hints: (*a*) Assume the dissolved CdS to be completely ionized. (*b*) From the low value of the secondary ionization constant it can be assumed that $[H^+]$ is practically equal to $[HS^-]$, although really $[H^+]$ is increased by a little $[H^+]$ from water and $[HS^-]$ is diminished by forming a trace of $[S^=]$. With this assumption that $[H^+] = [HS]$, the secondary ionization equation shows the value of $[S^=]$. (*c*) From the expression

$$\frac{[H^+]^2 \times [S^=]}{[H_2S]} = k_1 \cdot k_2$$

it is easy to find the value of $[S^=]$ when $[H^+]$ is known. The solubility product of CdS divided by the [S] gives the value of $[Cd^{++}]$.

90. At 25°C the ionization constant $k_1 \cdot k_2$ of H_2S into H ions and S ions is 1.1×10^{-22}. Calculate the concentration of sulfide ions in a solution which is 0.1 *M* in H_2S and 0.15 *N* in HCl.

91. If the solubility product of ZnS is 1.2×10^{-23} and a solution contains 0.2726 g of $ZnCl_2$ and 10 ml of 6 *N* $HC_2H_3O_2$ in 500 ml of solution: (*a*) how much $NaC_2H_3O_2 \cdot 3H_2O$ must be added to change the hydrochloric acid formed by precipitation of ZnS to acetic acid; (*b*) how much more $NaC_2H_3O_2 \cdot 3H_2O$ is required to repress the ionization of this acetic acid so that only 1 mg of Zn will remain in solution after treatment with H_2S; (*c*) what is the *p*H value of the solution after the ZnS precipitation has been accomplished by saturation with H_2S.

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[1] Magnifications of less than 10 diameters are often classed as macroscopic, although strictly speaking, they are not included in an exact definition of the term.

92. If acetic acid is 1.4 per cent ionized in 0.1 *N* solution, compute the ionization constant and the H-ion concentration in a 500-ml solution containing 6 g of $NaC_2H_3O_2 \cdot 3H_2O$ and 10 ml of 6 *N* acetic acid. What is the *p*H value of the solution?

93. If the solubility product of ZnS is 1.2×10^{-23} and of MnS is 1.4×10^{-15}, and if 500 ml of solution contains 0.0350 g of Zn and 0.695 g of Mn ions together with 6.0 g of $NaC_2H_3O_2$ and 60 milliequivalents of acetic acid, predict whether all the Zn and all the Mn will be precipitated when the solution is saturated with H_2S. Ionization constant of acetic acid is 1.8×10^{-5}; solubility product of H_2S, 1.08×10^{-23}.

CHAPTER XI

DETERMINATIONS OF CHLORINE, IRON, AND SULFUR IN SIMPLE SALTS

Determination of Chlorine in a Chloride

Place 1 g or more of the sample in a small, glass-stoppered weighing tube, weigh carefully to the nearest 0.1 mg, hold the tube over a clean 300-ml beaker, remove the stopper, and allow 0.2–0.3 g of the chloride to fall into the beaker. Replace the stopper and weigh again. The second weight will serve for the first weight of the second sample. All the analyses should be carried out in duplicate. Record the weighings in the notebook as shown on p. 194.

Dissolve the sample in 150 ml of water without heating, and add 8–10 drops of 6 N nitric acid. Calculate the volume of 0.1 N silver nitrate reagent required to precipitate the chloride on the assumption that the sample is pure sodium chloride; and add slowly, while stirring, 5 ml in excess of the calculated volume. Heat slowly, nearly to boiling, until the precipitate coagulates and the supernatant solution is clear, or allow to stand several hours in the dark. Test to see whether enough reagent was added, by pouring 5 ml more of silver nitrate without stirring. Keep the beaker from direct sunlight as much as possible, although the error resulting from exposure to light is slight.[1]

Filter through a weighed Gooch crucible and wash, first with water containing a little nitric acid until the test for silver with hydrochloric acid can no longer be obtained, and then twice with alcohol or water to remove the nitric acid. Dry the precipitate at 105–110° till a constant weight is obtained.

Alternative Procedure. If it is not desired to use a Gooch crucible for this determination, filter off the silver chloride upon an ashless, quantitative filter, wash as before, and dry at 100°. Transfer as much of the precipitate as possible to a weighed porcelain crucible, burn the filter

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[1] By exposure to light the silver is reduced photochemically. If the solution contains an excess of silver ions the error thus resulting is positive because chloride is set free by the reduction of the silver chloride and combines with more silver ions. If the silver ions are not in excess, the error is a negative one because the precipitate will weigh less when reduced. G. E. F. Lundell has shown that the errors are inappreciable in normal work where there is no great exposure to light.

(as described on p. 178), and add the ash of the filter to the main portion of the precipitate. Moisten with a little nitric acid and a drop or two of concentrated hydrochloric acid, dry on the water bath, and heat over a free flame until the silver chloride *begins* to melt. Weigh after cooling in a desiccator. Report the percentage of chlorine present.

Remark. Instead of drying the Gooch crucible and its contents in the oven heated to 105–110° it is a little quicker and nearly as accurate to dry by washing with alcohol and ether. After having removed all the soluble salts by washing with hot water, wash the contents of the crucible with four 5-ml portions of alcohol and then four times with 5-ml portions of ether. After this draw air through the crucible for 5 minutes, wipe the outside of the crucible dry, allow it to remain 15 minutes in a desiccator over calcium chloride, and weigh promptly. Before using the crucible for filtering, dry it by the same treatment with alcohol and ether and standing in the desiccator. This method of handling precipitates has proved very popular.

Solubility of Silver Chloride. One liter of water dissolves 0.00154 g AgCl at 20° and 0.0217 g at 100°. In water containing a *little* hydrochloric acid, the AgCl is less soluble than in pure water, but as the quantity of hydrochloric acid is increased, the solubility of AgCl rises rapidly. Thus 1 l of 1 per cent HCl dissolves only 0.0002 g AgCl at 21°, but 1 l of 5 per cent HCl dissolves 0.0003 g and 1 l of 10 per cent HCl dissolves 0.0555 g AgCl. By melting the silver chloride there is always loss by volatilization.

Computation. The fraction, usually expressed as a decimal, which represents the amount of an element A in one of its compounds is commonly called the *chemical factor:* It represents the weight of A in one part by weight of the compound, irrespective of the unit of weight. It expresses the ratio of the desired weight of A to the weight of the precipitate obtained.

Thus, to be specific, 1 g of silver chloride contains 0.7526 g of silver; 1 lb of silver chloride contains 0.7526 lb of silver. If p g of silver chloride are obtained from s g of original substance, then $0.7526\,p$ is the weight of silver in the sample taken and $(0.7526p \times 100)/s$ = percentage of silver in the substance analyzed. The general rule for computing a direct gravimetric analysis is as follows: Multiply the weight of the precipitate by 100 times the chemical factor and divide by the weight of the original substance. Using the notation as above:

$$\frac{p \times \text{chemical factor} \times 100}{s} = \text{desired percentage}$$

A table of chemical factors is given at the back of the book. The use of the table may be illustrated by an example:

From 0.5 g of arsenic ore, 0.4761 g of $Mg_2As_2O_7$ was obtained. What is the percentage of arsenic in the ore?

In the table, we seek As under the heading " Sought " and $Mg_2As_2O_7$ under the heading " Found," and we find on the same line that the chemical factor is 0.4827.

Finally, in the fourth column we find that the logarithm of this number multiplied by 100 is 1.6837. The computation is as follows:

log factor × 100	1.6837
log 0.4761	9.6777 − 10
colog 0.5	0.3010
	1.6624 log of 45.96

The ore contains 45.96 per cent of arsenic.

If the weight of ore had been 0.4827 g (a so-called *factor* weight) the percentage of arsenic would have been found by multiplying the weight of precipitate by 100.

This table of factors is convenient, but every chemist should know how to compute any factor. As this often causes trouble for beginners, the method of computing the factors will be discussed.

Computing the Factor. The symbol AgCl shows that 1 atomic weight of silver, 107.88, is present in 1 molecular weight of silver chloride, 143.34. This ratio of weights is independent of the unit of weight used and is just as true of tons, pounds, ounces, or grains as it is of grams. Using the conception of the gram-molecular weight, the formula shows that 107.88 g of silver is present in 143.34 g of silver chloride. If 143.34 g of silver chloride contains 107.88 g of silver, 1 g of silver chloride will contain 107.88 ÷ 143.34 = 0.7526 g silver. In other words, the chemical factor for silver in silver chloride is found by dividing the atomic weight of silver by the molecular weight of silver chloride. Using symbols, the chemical factor is Ag/AgCl. It represents the ratio of *what is sought to what has been found.*

In the arsenic analysis referred to above, the symbol for magnesium pyroarsenate, $Mg_2As_2O_7$, shows that 2 atoms of arsenic are present in the molecule. The chemical factor is $2As/Mg_2As_2O_7 = 149.9 \div 310.6 = 0.4827$.

As a still more complicated example, assume that a sample of magnetite is analyzed in such a way that all the iron is converted into Fe_2O_3 and it is desired to know the weight of Fe_3O_4 originally present. The chemical factor for converting a weight of Fe_2O_3 into the equivalent weight of Fe_3O_4 is $2Fe_3O_4/3Fe_2O_3 = 463.1 \div 479.1 = 0.9666$.

The concept of the *chemical factor* may be applied to any chemical equation as well as to any precipitate. The following equation represents the reaction between ferrous ions and dichromate ions:

$$6Fe^{++} + Cr_2O_7^{--} + 14H^+ \rightarrow 6Fe^{+++} + 2Cr^{+++} + 7H_2O$$

On the basis of this equation we can compute the weight of ferrous ammonium sulfate which will react with a given weight of potassium dichromate. The chemical factor is

$$\frac{6[FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O]}{K_2Cr_2O_7} = \frac{6 \times 392.1}{294.2} = 7.998$$

If the weight of dichromate is multiplied by this factor the product will be the equivalent of ferrous ammonium sulfate.

Record the results obtained in the above analysis in the notebook as follows:

Date...............

DETERMINATION OF CHLORINE IN CHLORIDE, SAMPLE NO.

	No. 1	No. 2
Weight sample and tube	16.1721 15.9976	15.9976 15.7117
Weight sample	.1745	.2859
Weight crucible + precipitate	14.4496	15.6915
Constant weights	14.4487 14.4485	15.6915
Weight crucible	14.2216	15.3196
Constant weight	14.2216	15.3194
Weight AgCl	.2269	.3721
Log weight AgCl	9.3558–10	9.5706–10
Log factor $\frac{Cl}{AgCl} \times 100$	1.3934	1.3934
Colog sample	0.7583	0.5438
	1.5075	1.5078
Cl in sample No.	32.19%	32.20%
Average	32.20	

Determination of Iron and Sulfur in Ferrous Ammonium Sulfate

The determination of iron is one of the best known of all the gravimetric methods of analysis, and for many years it has been the custom to require most students of analytical chemistry in the colleges of the United States to carry out an analysis of ferrous sulfate or of ferrous ammonium sulfate. In a sulfate solution, some basic ferric sulfate is often formed if the precipitation of ferric hydroxide is accomplished by merely neutralizing with ammonia. It is the general practice, therefore, to dissolve the first precipitate in acid and repeat the precipitation with ammonia.

It has been shown, however, that the formation of basic sulfate can be prevented if a considerable excess of ammonium hydroxide is used.

Procedure. Weigh out, to the nearest milligram, duplicate portions of 0.7–1 g into 400-ml beakers. Moisten the sample with 5 ml of 6 *N* hydrochloric acid, dilute with 5 ml of water, and heat, if necessary, to dissolve the sample. Heat nearly to boiling, and to the hot solution add concentrated nitric acid, drop by drop, until all the iron is ozidized to the ferric condition. When the iron is partially oxidized, the nitric oxide combines with the excess of ferrous salt, forming a dark brown, unstable compound. Continue adding the nitric acid until the dark color fades and a clear yellow solution is obtained. Not more than 2 ml of nitric acid should be necessary.[1] Boil gently for about 3 minutes to remove the reduced nitrous compounds. Dilute to about 200 ml and neutralize with ammonium hydroxide,[2] finally adding 5–7 ml of concentrated ammonium hydroxide in excess. Heat carefully to about 70° and allow the precipitate to settle.

Decant the clear solution through a paper filter which has an ash of less than 0.1 mg. Filters with 9-cm diameter are large enough for all the gravimetric methods of this book except in this procedure when too much is taken. Be sure not to use a paper such as is used in qualitative analysis, which has not been washed with hydrofluoric acid to make it ashless. The use of suction is inadvisable because suction drags particles of the gel into the pores of the paper and clogs it; when a gelatinous precipitate is drained by suction, it usually cracks and the wash liquid does not then come in contact with all parts of the precipitate. After the clear solution has been poured off, stir up the precipitate well with about 50 ml of hot water, let the precipitate settle, and again decant off as much as possible of the clear liquid. Repeat this operation, called *washing by decantation*, once more before attempting to transfer the precipitate to the filter. Finally, wash all the precipitate onto the paper (cf. p. 173) and use a *policeman* at the last. Wash with hot water from the wash bottle, paying special attention to the top of the filter paper, which should fit closely to the funnel, until about 3 ml of the last washing, collected as it runs through the funnel, gives no test for chloride when acidified with HNO_3 and treated with $AgNO_3$ solution. Discard the test portions but do not test until the paper has been washed at least six times. Save the filtrate and all the washings, except the small portions taken for the chloride tests, for the determination of sulfate.

Meanwhile, ignite and cool in a desiccator a 25-ml porcelain crucible. When it is at the room temperature, weigh the crucible to the nearest 0.1 mg and record the weight of the empty crucible in the notebook. Fold the top of the paper over the moist precipitate, and transfer the paper and its contents in an inverted position to the weighed crucible. If necessary, wipe the sides of the funnel with a piece of ashless paper and add this paper to the contents of the crucible. Be sure that there is filter paper between the precipitate and the outer air, to avoid loss of precipitate when the moisture is expelled. Heat carefully over a small flame placed in front of the crucible until the paper is dry (see p. 181). At the start take care that there is no spattering. When the precipitate is dry and the paper begins to decompose, move the flame to the base of the crucible and gradually raise the temperature a little, but do not let the paper take fire. Occasionally change the postion of the crucible, kept on its side with free access of air, so that different parts of the walls of the crucible are nearest to the flame. Keep the flame fairly low until all the paper is consumed and there are no more shiny, black spots on the side of the crucible. Finally set the crucible upright and expose to the full heat of a Tirrill burner for a few minutes. During the heating the following reaction takes place:

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[1] Bromine or hydrogen peroxide can be used instead of nitric acid. If a black iron precipitate is obtained later, owing to incomplete oxidation, add 10 ml of 3 per cent hydrogen peroxide and heat till the precipitate is reddish brown.

[2] Ammonia kept in glass bottles for any length of time contains silica and gives high results. Freshly distilled ammonia is best for this analysis and in no case should ammonia be used from a bottle containing any turbidity: filtering this ammonia is not sufficient. Filters used in quantitative analysis should not have more than 0.05 mg ash. Distilled ammonia can be kept in paraffin-lined bottles.

$$2[Fe(OH)_3 \cdot xH_2O] \rightarrow Fe_2O_3 + (2x + 3)H_2O$$

It is always best not to overheat a precipitate until all the filter paper is consumed and the tar deposits are burned off. If the heat is raised too quickly, the hot carbon from the paper is likely to reduce some of the ferric iron to magnetite, Fe_3O_4, which is the most stable oxide of iron and cannot be converted to Fe_2O_3 by heating in the air. Moreover, sometimes the ash of a precipitate fuses a little, and the fusion product may enclose a little unburned carbon which will prevent its oxidation.

Allow the crucible to cool a minute or two in the air, transfer to a desiccator containing a little fused calcium chloride or other desiccant, and after 15 minutes weigh to the nearest 0.1 mg. Heat the crucible for 5 minutes more over the full heat of the burner, cool as before, and weigh again. Repeat these operations until two consecutive weights agree within 0.3 mg. Remember that the weight will always be too low if the crucible feels warm to the fingers. From the weight of the Fe_2O_3 calculate the percentage of iron present.

Remarks. It is not advisable to heat the precipitate over the blast because Fe_3O_4 is formed at high temperatures. This magnetic oxide is also formed if the carbon of the filter is not consumed at a low temperature. When once formed it is very difficult to get it back to the less stable Fe_2O_3. The color of the ignited oxide does not indicate the presence of magnetite, for pure ferric oxide is nearly black after strong ignition. The ignited oxide is difficultly soluble in dilute hydrochloric acid but can be dissolved by long digestion with concentrated hydrochloric acid on the water bath.

Several errors are possible in making the chloride test: (1) the test may be made too soon, so that desired material is lost from the filtrate used in making the test. (2) The test may be obtained from a little chloride solution on the outside of the funnel which has been allowed to dip into the solution. (3) The test may be obtained because the wash water or the nitric acid contains a little chloride, probably because a careless student has mixed the stoppers of the acid bottles or the laboratory assistant may have been careless in filling the bottles. To guard against this error test the water and the acid with silver nitrate, throwing away the acid if it is found to contain chloride. (4) The test will not be obtained unless the solution is made acid with nitric acid, because silver chloride is soluble in ammonia solution.

If the chloride is not removed by careful washing, the ammonium chloride will react with the ferric hydroxide upon heating and ferric chloride will be formed which is volatile at the ignition temperature.

Platinum crucibles can be used in this analysis, but the results obtained are no better than when porcelain crucibles are used. The chief cause of high results is impure ammonia. It is not sufficient to filter the ammonia solution, because, when sediment is found in the reagent, the solution is saturated with silica which is deposited when the ammonia is added to an acid solution.

Determination of Sulfate

Take the filtrate from the iron determination,[1] neutralize with hydrochloric acid, and add 4 ml of 6 *N* acid in excess. Heat to boiling, and add to the hot solution, while stirring, 135 ml of boiling-hot, tenth-normal barium chloride solution. Allow the solution to stand half an hour, preferably in a warm place, and test, to see whether the precipitation was complete, by adding a little more reagent. Filter, wash free from chloride with hot water, ignite, and weigh as $BaSO_4$. If a Gooch crucible is used, dry it first at 110° and later heat the crucible in an air bath to about 300°. Dry and heat the precipitate in the same way. A suitable air bath can be made with a piece of thin sheet iron made into a cone with about 2.5-in. base. Place a triangle on top of the inverted cone to hold the crucible, and heat with a burner under the apex of the cone.

Report the percentage of sulfur in the sample.

Errors Which May Occur in the Precipitation of Barium Sulfate. *I. In the Precipitation of Barium Chloride with Pure Sulfuric Acid.* If a dilute, slightly acid solution of barium chloride is treated at the boiling temperature with an excess of dilute sulfuric acid, the precipitate contains all the barium except a very small, negligible amount. If, however, the precipitate is weighed, the result is invariably too low; and this is true even when the solution is evaporated to dryness in order to recover the last traces of barium. The precipitate always contains barium chloride in a form which cannot be removed by washing. A mixture, therefore, of barium sulfate and barium chloride is weighed, and as the molecular weight of the chloride is less than that of the sulfate, the result must be too low. To obtain accurate results, the chlorine combined with barium in the precipitate must be replaced by SO_4; and this can be accomplished by moistening the precipitate with concentrated sulfuric acid, and heating until the excess of the acid is removed by volatilization.

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[1] If the filtrate is lost, or the analysis is to be repeated, dissolve a fresh sample of 1 g in 2 ml of 6 *N* hydrochloric acid and 400 ml of water. Proceed as above described without oxidizing or removing the iron, but add the barium chloride more slowly.

Not only is barium *chloride* carried down with barium sulfate, but all barium salts as well, especially the chlorate and nitrate. These are, however, readily changed to sulfate by the above treatment with concentrated sulfuric acid. It is immaterial in the estimation of barium how the precipitation is effected; whether the sulfuric acid is added quickly, or drop by drop, the results are always the same.

II. In the Precipitation of Pure Sulfuric Acid with Barium Chloride. This is the reverse process, but here it is not a matter of indifference whether the barium chloride is added slowly, drop by drop, or rapidly all at one time. In the first instance, the results are very near the truth without the application of any correction; in the second, too high results are obtained, because by the rapid addition of the reagent more barium chloride is carried down with the precipitate than when the reagent is added very slowly.

To obtain the true weight of barium sulfate, it is often necessary to make a deduction for the amount of barium chloride contained in the precipitate and to add the weight of barium sulfate remaining in solution.

The chlorine contained in the precipitate can be determined in several different ways.

1. Fuse the precipitate with 4 times as much pure sodium carbonate, extract the melt with hot water, filter, make the filtrate acid with nitric acid, and precipitate the chlorine with silver nitrate. Filter and weigh.

2. Still more accurate is the process of Hulett and Duschak.[1] Place the ignited precipitate of barium sulfate in a U-tube of which one arm is drawn out into a thin, right-angled, gas delivery tube. Add concentrated sulfuric acid to the precipitate and heat the mixture by placing the U-tube in hot water. The barium sulfate dissolves readily in the hot, concentrated sulfuric acid, and the barium chloride present is decomposed. To determine the amount of hydrochloric acid set free, pass a slow stream of air, which has been washed with caustic potash solution, through the tube, with the drawn-out end of the tube dipping into a stout test tube containing 0.01 N silver nitrate solution. After 2–2.5 hours all the hydrochloric acid will have been expelled from the sulfuric acid.

Remove the decomposition apparatus, rinse out the gas delivery tube with a little water, and determine the silver remaining in solution volumetrically (cf. Volhard method).

For the determination of the dissolved barium sulfate, evaporate to dryness the filtrate from the first precipitation, moisten the residue with a few drops of concentrated hydrochloric acid, take up with water, filter off the slight precipitate of barium sulfate, and weigh. During all such work take care to prevent sulfuric acid contamination from the air in the laboratory. The evaporation should, therefore, take place on the steam bath or steam-table.

Calculation of the True Weight of Barium Sulfate. If the weight of the first precipitate of crude barium sulfate is a, the weight of the barium chloride contained in this precipitate, as determined by titration of the amount of chlorine, is b, and the amount of barium sulfate in solution is c, then $a - b + c$ represents the weight of pure barium sulfate.

Experience has shown, however, that, when pure sulfuric acid is precipitated by means of dilute barium chloride solution added drop by drop, the errors b and c are approximately equal and counterbalance each other so that the weight a is very close to that of the pure barium sulfate.

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[1] *Z. anorg. Chem.*, **40**, 196 (1904).

III. In the Precipitation of Sulfates with Barium Chloride. Here the relations are far more complicated than in the precipitation of pure sulfuric acid, partly because the barium sulfate is more soluble in salt solutions than in water containing a little acid, and partly because of the tendency of barium sulfate to occlude not only barium chloride but many other salts as well. Solutions of chromium sulfate are either violet or green. From the boiling-hot green solution only one-third of the sulfuric acid is precipitated, the remainder probably being present in the form of a complex chromium sulfate cation;[1] on cooling, the green solution gradually becomes violet, and after some time all the sulfuric acid is precipitated. The precipitation of barium sulfate in the presence of ferric iron has been much studied. In the boiling-hot solution, not all the sulfuric acid is precipitated and considerable iron is thrown down with the barium sulfate, and furthermore, the precipitate then loses SO_3 on ignition. Since ferric oxide weighs less than an equivalent weight of barium sulfate sometimes the results are as much as 10 per cent too low. On the other hand, Küster, and Thiel[2] were able to get satisfactory results (1) by precipitating the sulfuric acid from such a solution in the cold, (2) by slowly adding the ferric chloride and sulfuric acid solution to the hot solution of barium chloride, or (3) by precipitating the iron by an excess of ammonia, heating, adding barium chloride to the solution without filtering off the ferric hydroxide, and finally dissolving the ferric hydroxide in dilute hydrochloric acid.

Most chemists, however, deem it advisable to remove trivalent metals before attempting to determine the sulfuric acid. This is accomplished in the case of ferric iron by adding a liberal excess of ammonia to the dilute, slightly acid solution which is at a temperature of about 70°. If 5–7 ml of concentrated ammonia (*d* 0.90) is added in excess of the amount required for neutralization,[3] the precipitate is not likely to contain any basic ferric sulfate. If, on the other hand, the solution is barely neutralized with ammonia, the precipitate will invariably contain some sulfate.

The bivalent metals are occluded to a much less extent, so that it is not, as a rule, necessary to remove them. On the other hand, in the presence of considerable amounts of bivalent metal with relatively small amounts of sulfuric acid, the error arising from occlusion is likely to be large, so that it is better to remove the bivalent metals. The error caused by ferric salts can be largely overcome by reducing the iron with zinc.

In the presence of alkali nitrate or chlorate the barium sulfate precipitate will contain considerable quantities of barium chlorate and nitrate which it is impossible to remove by washing with hot water. These acids, therefore, must be decomposed by evaporation with hydrochloric acid before the precipitation of the sulfuric acid is attempted.

In ordinary chemical practice it is usually a question of determining sulfuric acid in a solution containing considerable amounts of ammonium or alkali chloride, ammonium or alkali sulfate, and some free hydrochloric acid. Now ammonium and alkali sulfates are also occluded by barium sulfate, and the amount of occlusion increases as the solution is more concentrated with respect to these substances. For this reason it is evident that barium sulfate should always be precipitated in a dilute solution. On the other hand, if the solution is too dilute or very concentrated the crystals are so small that they will run through a filter. A small amount of free hydrochloric acid is indispensable, but larger amounts have a solvent effect upon the precipitate. One might think that adsorbed ammonium chloride would do no harm, but it has been found to cause some volatilization of sulfate during ignition.

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[1] Recoura, *Compt. rend.*, **113**, 857; **114**, 477.

[2] *Z. anorg. Chem.*, **22**, 424.

[3] Pattinson, *J. Soc. Chem. Ind.*, **24**, 7.

For an amount of sulfuric acid corresponding to 1–2 g of barium sulfate, the precipitation should take place in a volume of 350–400 ml and in the presence of 1 ml of 12 N hydrochloric acid.

If a *neutral* solution is at hand, dilute to a volume of 350 ml and add 1 ml of concentrated hydrochloric acid. Carefully neutralize an *alkaline* solution with hydrochloric acid, using methyl orange as indicator, add 1 ml of concentrated hydrochloric acid in excess, and dilute the solution to 350 ml.

Finally, in the case of an *acid* solution, either evaporate to dryness, moisten the residue with 1 ml of concentrated hydrochloric acid, and add 350 ml of water, or, with methyl orange as indicator, neutralize the solution with ammonia, add 1 ml of concentrated hydrochloric acid, and dilute to 350 ml.

Remarks. In the presence of ammonium salts the precipitation of the barium sulfate should not be accomplished by the slow addition of the barium chloride, as is otherwise desirable, for, as Hintz and Weber have shown, this leads to low results, whereas the occlusion caused by the rapid addition of the barium chloride counterbalances this error.

Under no circumstances should a precipitate of barium sulfate be heated over a blast lamp, for then sulfuric anhydride is evolved from the barium sulfate.

To explain the occlusion of barium chloride by barium sulfate, Hulett and Duschak[1] suggested that perhaps the precipitate might contain salts such as $BaCl{\cdot}HSO_4$, $(BaCl)_2SO_4$, and $Ba(HSO_4)_2$, and Folin[2] believed that this was so because some of his precipitates lost SO_3 on ignition while others lost HCl. He also suggested the possibility of salts such as $Ba(KSO_4)_2$ being precipitated.

HOME PROBLEMS

94. Calculate the chemical factors for converting weights of (*a*) silver chloride into chlorine, (*b*) ferric oxide into iron, (*c*) barium sulfate into sulfur, (*d*) magnesium pyrophosphate into magnesium oxide, and (*e*) magnesium pyrophosphate into phosphoric anhydride. How many grams of Mn_3O_4 can be obtained from 2 g of MnO_2?

95. What weight of sulfur corresponds to 5.672 g of barium sulfate? Find the percentage of SO_3 in pure Mohr's salt, $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$.

96. Compute the volume of 0.1 N silver nitrate required to precipitate the chlorine in 0.26 g of sodium chloride. How much reagent would be required containing 25 g of silver nitrate per liter?

97. From the tables at the back of the book, compute the volume of ammonia solution, d 0.96, required to neutralize a solution obtained by pouring 35 ml of sulfuric acid, d 1.75, into 200 ml of water.

Note. The actual weight of H_2SO_4 taken is obtained by multiplying the volume by the density (weight of 1 ml) and by the percentage of H_2SO_4 by weight. The neutralization reaction is

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

From the weight of H_2SO_4 the weight of NH_3 required is obtained by multiplying by the ratio $2NH_3/H_2SO_4$. Finally the volume of NH_3 required is obtained by dividing the requisite weight of NH_3 by the weight of NH_3 in 1 ml of the reagent, which is found by multiplying its density by the percentage of NH_3 by weight. The problem can be set up as follows:

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[1] *Loc. cit.*

[2] *J. Biol. Chem.*, **1**, 131 (1905).

$$\frac{\text{ml } H_2SO_4 \times d \text{ of } H_2SO_4 \text{ solution} \times \%H_2SO_4 \text{ by weight} \times 2NH_3}{d \text{ of } NH_3 \text{ solution} \times \%NH_3 \text{ by weight} \times H_2SO_4} = \text{ml required of } NH_3 \text{ solution}$$

98. In the analysis of an iron ore from which a pure precipitate of $Fe(OH)_3$ is obtained, what weight of sample should be taken so that each centigram of ignited Fe_2O_3 will represent 0.1 per cent of iron present? What weight of impure ferrous salt so that the weight of pure $BaSO_4$ obtained divided by 0.05 will give the percentage of sulfur present?

99. What weight of magnetite must be taken for analysis so that the weight of Fe_2O_3, obtained from it and containing all the iron, multiplied by 100, will give the percentage of Fe_3O_4 in the sample?

100. A mixture of pure LiCl and $BaBr_2 \cdot 2H_2O$ weighing 0.6 g gives a precipitate of insoluble silver salt weighing 1.35 g. Find the percentage of bromine present.

101. A mixture of LiCl and KCl weighing 0.15 g is obtained in the analysis of 0.48 g of a silicate. The silver chloride precipitate obtained from the above weight of chlorides weighed 0.42 g. Compute the percentages of K_2O and Li present in the silicate.

102. A sample of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ weighing 1.2 g is dissolved in water containing 2 ml of 6 N hydrochloric acid. Compute: (*a*) the volume of concentrated nitric acid, d 1.42 (see table at the back of the book), required to oxidize the iron if the nitric acid is reduced to NO; (*b*) the volume of ammonia solution, d 0.90 (see table), required to neutralize the solution and precipitate the iron as $Fe(OH)_3$; and (*c*) the weight of the resulting precipitate after ignition to Fe_2O_3.

Note. The equation for oxidizing the Fe^{++} is

$$3Fe^{++} + NO_3^- + 4H^+ \rightarrow 3Fe^{+++} + NO + 2H_2O$$

and the chemical factor for converting $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ into HNO_3 is $\frac{HNO_3}{3[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]} = \frac{63}{3 \times 392}$. This shows that very little HNO_3 is actually reduced. On the other hand, *dilute* HNO_3 solutions have very little oxidizing power so that in practice the actual quantity of oxidant required is considerably in excess of that shown by the above computation. The equation also shows that some acid, in addition to the reduced HNO_3, is necessary to keep the oxidized iron in solution. In computing the volume of NH_3 required, proper allowance for the 3 molecules of HCl used up during the oxidation can be made by assuming that each molecule of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ takes only 2 moles of NH_3. The above problem is interesting, but in practice it is best to add sufficient NH_3 to neutralize all HCl and HNO_3 added and allow 3 moles of NH_3 for each atom of Fe.

103. In the determination of sulfur in pyrite, what weight of sample should be taken so that the weight of $BaSO_4$ precipitate in centigrams when divided by 4 gives the percentage of sulfur in the sample?

104. What weight of impure ferrous ammonium sulfate should be taken so that the number of centigrams of $BaSO_4$ will be 5 times as large as the percentage of S present?

105. A sample of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ contains glass as the only impurity. If, from 0.7650 g of the solid, 0.1263 g of Fe_2O_3 was obtained, how many milliliters of 2.5 per cent $BaCl_2 \cdot 2H_2O$ solution will be required to precipitate the S in the filtrate from $Fe(OH)_3$? What percentage of glass was present?

CHAPTER XII

PHOSPHORIC ACID IN APATITE. ANALYSIS OF LIMESTONE OR PORTLAND CEMENT

The phrases *phosphoric acid in apatite* and *phosphorus pentoxide in apatite* require a word of explanation. According to the ideas that prevailed during the greater part of the nineteenth century and earlier, oxygen was the acid substance (German, *Sauerstoff*) common to all acids. In the terms of the dualistic theory of Berzelius, which was the forerunner of the dissociation theory of Arrhenius (1887), there were two kinds of oxides — basic or positively charged oxides, and acidic or negatively charged oxides. Salts were compounds of these two kinds of oxides. Thus sodium carbonate was written $Na_2O{\cdot}CO_2$, and sodium sulfate $Na_2O{\cdot}SO_3$. Moreover, CO_2 was commonly called carbonic acid and SO_3 sulfuric acid. A substance like hydrogen chloride was not considered to be a true acid because it contained no oxygen, and a salt like sodium chloride was not considered to be a true salt by the followers of Berzelius; these were merely binary compounds.

The analytical chemist today often reports the results of analysis in terms of the old dualistic theory. In the analysis of sodium carbonate, for example, he still computes the percentage of " soda," Na_2O, and of " carbonic acid," CO_2. This may be partly due to the fact that the analytical chemist is a practical person and not always interested in theoretical hypotheses as much as in methods of analysis. One of the best-known works on analytical chemistry in an edition published in the latter part of the nineteenth century used an old abandoned nomenclature probably because the author had never accepted the modern theories. That is, however, not the main reason why the chemist clings to the old-fashioned method of reporting his results; there are two other more important reasons. In the first place, there is a very large accumulation of analytical data concerning the chemical composition of minerals and rocks. The older data often have to be recomputed on the basis of our present ideas concerning atomic weights, but it would be confusing to many mineralogists if the chemist were to change his method of reporting results. In the second place, the analysis of a substance like sodium carbonate, or of a mineral, never involves the direct determination of the element oxygen. It is better to distribute the oxygen among the various elements rather than to determine it by difference or to assign it to a single constituent. It is fairer to assign one oxygen to each two atoms of sodium and two to each atom of carbon in sodium carbonate than to report the percentage of Na and of CO_3. In a mineral such as $KAlSi_3O_8$, the potassium, the aluminum, and the silicon are actually determined by analysis. Unless one knew that the mineral analyzed was feldspar, he would have no idea how many atoms of oxygen to write in combination with the silicon. By reporting the analysis in terms of K_2O, Al_2O_3, and SiO_2 the oxygen is taken care of very nicely. With a mineral like apatite, $[Ca_3(PO_4)_2]_3{\cdot}CaFCl$, there is difficulty, however, for if the calcium is reported as CaO the analysis will total over 100 per cent if every constituent is determined. In such cases the analyst sometimes does report all the calcium as CaO and after summing up his results writes " less oxygen equivalent to chlorine and fluorine." In other words, the analyst cannot tell at all, unless he has some knowledge of minerals, how the chlorine and fluorine are combined. He knows, however, that the chlorine and fluorine are probably present as chloride and fluoride, and if he has computed all the basic constituents as oxides he has used 8 parts by weight of oxygen (one-half atomic weight) for each 19 parts by weight of fluorine (one atomic weight) and for each 35.46 parts by weight of chlorine. When we say that we determine the phosphoric acid in apatite, therefore, we are unconsciously using the discarded nomenclature of Berzelius. It were better to say that we determine the phosphorus content expressed in terms of phosphorus pentoxide.

The spelling of the word *phosphorus* is often a stumbling-block for beginners. When spelt in this way, this word signifies a noun and the name of an element. The spelling *phosphorous* indicates, on the other hand, an adjective. Phosphorous acid is always H_3PO_3, but there are several other acids containing *phosphorus*.

The determination of phosphorus in apatite is an interesting problem. The mineral dissolves by heating with mineral acid because HPO_4^{--} and $H_2PO_4^-$ are ions which are very slightly dissociated. $H_2PO_4^-$, as we have already seen, is dissociated into H^+ and HPO_4^{--} enough to affect phenolphthalein indicator but not enough to affect methyl orange. Apatite, when placed in contact with water, tends to form a saturated solution of calcium phosphate, and this salt is ionized into PO_4^{---} and Ca^{++}. But PO_4^{---} cannot exist in the presence of a large quantity of H^+ except in accordance with the mass-action law.

$$\frac{[H^+]\,[PO_4^{---}]}{[HPO_4^{--}]} = 3.6 \times 10^{-13}$$

and similarly

$$\frac{[H^+]\,[HPO_4^-]}{[H_2PO_4]^-} = 2.0 \times 10^{-7}; \quad \frac{[H^+] \times [H_2PO_4^-]}{[H_3PO_4]} = 1.1 \times 10^{-2}$$

By treatment of calcium phosphate with an excess of mineral acid, therefore, the sample dissolves, forming Ca^{++} ions, H_3PO_4, and some $H_2PO_4^-$.

The usual method of determining phorphorus present as phosphate is to get a precipitate of magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, which upon ignition yields magnesium pyrophosphate, $Mg_2P_2O_7$.

To obtain the precipitate it is necessary to make the solution ammoniacal. In the analysis of phosphate which is soluble in water, this presents no difficulty, but with calcium phosphate, as soon as the acid solution is neutralized, calcium phosphate will precipitate.

There are three ways in which the phosphate can be separated from calcium. The first involves the addition of tin to the nitric acid solution, whereupon phosphoric acid is carried down with the metastannic acid precipitate that forms. This method is not popular in quantitative analysis because the precipitate is hard to filter. Another way is to add considerable ferric salt to the solution and make a basic acetate precipitation at about $pH = 9$, in which case ferric phosphate is precipitated together with basic ferric acetate. This precipitate can be washed free from calcium, dissolved in an acid, and, if citric or tartaric acid is added to the solution, it can then be made ammoniacal without any precipitation of the iron or of the phosphate. This method has been used for quantitative work and is a little easier than the tin method. The favorite method of precipitating phosphoric acid from an acid solution is by means of ammonium molybdate. In a solution of the proper acidity and with a suitable content of ammonium salt, the phosphoric acid is precipitated as the ammonium salt of phosphomolybdic acid, in which, under favorable conditions, there are 12 molecules of molybdic acid anhydride combined with 1 of ammonium phosphate. The formula of the compound is usually written $(NH_4)_3PO_4 \cdot 12MoO_3$. It forms a yellow precipitate with even very small quantities of phosphorus. It is easily dissolved by dilute alkali hydroxide and is least soluble in dilute acid containing ammonium salt. The precipitate can be washed free from other substances in the original acid solution, dissolved in ammonia water, and, from the ammoniacal solution, a precipitate of magnesium ammonium phosphate obtained upon the addition of "magnesia mixture," which is magnesium chloride solution containing sufficient ammonium salt to prevent the precipitation of magnesium hydroxide when the reagent is added to an ammoniacal solution.

The reactions that take place in this analysis are the following:

$$\mathbf{Ca_3(PO_4)_2} + 6H^+ \rightarrow 3Ca^{++} + 2H_3PO_4$$

$$3NH_4^+ + H_3PO_4 + 12MoO_4^{--} + 21H^+ \rightarrow \mathbf{(NH_4)_3Mo_{12}PO_{40}} + 12H_2O$$

$$\mathbf{(NH_4)_3Mo_{12}PO_{40}} + 23NH_3 + 12H_2O \rightarrow HPO_4^{--} + 12MoO_4^{--} + 26NH_4^+$$

$$HPO_4^{--} + NH_3 + Mg^{++} + 6H_2O \rightarrow \mathbf{MgNH_4PO_4 \cdot 6H_2O}$$

$$2(\mathbf{MgNH_4PO_4 \cdot 6H_2O}) \rightarrow \mathbf{Mg_2P_2O_7} + NH_3 + 13H_2O$$

Determination of P_2O_5 in Apatite

Weigh out duplicate portions of the finely powdered mineral of 0.2–0.25 g, taking care to get the nearest tenth of a milligram as accurately as possible. Heat in a covered 200-ml casserole with 15 ml of 6 *N* nitric acid. Evaporate to dryness on the steam bath or hot plate, taking care to avoid spattering. Heat the residue for at least 15 minutes at 110–120° to dehydrate silica. Digest the residue with 25 ml of 6 *N* nitric acid, and heat a few minutes to dissolve the soluble material. Filter and wash with small portions of hot water, receiving the filtrate and washings in a 300-Erlenmeyer flask. Continue to wash until 5 ml of the filtrate will give no precipitate of calcium phosphate when neutralized with ammonia. If a precipitate is obtained, pour the test back into the filtrate. The volume of the solution should not exceed 100 ml at this point.

To the filtrate, carefully add 6 *N* ammonium hydroxide solution until a slight permanent precipitate is produced of calcium phosphate. Dissolve this by adding a few drops of 6 *N* nitric acid. Heat the solution to about 65°, and add 75 ml of ammonium molybdate reagent.[1] Keep the solution at this temperature for half an hour, filter, and wash once by decantation with an acid solution of ammonium nitrate[2] and at least six times on the filter. When the washing is complete place the flask containing the bulk of the precipitate under the funnel and allow 6 *N* ammonium hydroxide solution to drop upon the upper edge of the filter from a buret, until enough has been added to dissolve all the precipitate on the filter paper and that in the flask. Rotate the contents of the flask from time to time and avoid using an unnecessary excess of ammonia. Wash the filter paper thoroughly with hot water. The volume should not exceed 200 ml at this point. Drop a piece of sensitive litmus paper into the solution and add 6 *N* hydrochloric acid, with constant rotation of the flask, until the litmus paper in the solution turns pink. Add 10 ml of magnesia mixture[1] and heat almost to the boiling point. Add 2–3 drops of phenolphthalein indicator, and neutralize with 1.5 *N* ammonium hydroxide until the solution is colored pink by the indicator. Cool, add one-fifth of the solution's volume of concentrated ammonium hydroxide, and allow to stand for at least 4 hours. Continue the analysis by any one of the following three methods.

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[1] See p. 249 for the composition of the reagent. If the slightly ammoniacal reagent is preferred, omit the neutralization with NH_4OH.

[2] Mix 100 ml of 6 *N* ammonium hydroxide with 325 ml of 6 *N* nitric acid and dilute with 100 ml of water.

(a) **Weighing as $MgNH_4PO_4 \cdot 6H_2O$.** Prepare a Gooch crucible with a suitable asbestos mat for filtering. Rinse out the crucible under gentle suction, with four 5-ml portions of alcohol followed by four 5-ml portions of ether. Draw air through the crucible for 5 minutes to evaporate the ether, wipe off the outside with a clean cloth, allow to stand in a desiccator over calcium chloride for 15 minutes, and then weigh carefully. Decant off the mother liquor from the magnesium ammonium phosphate precipitate through this weighed crucible, wash the precipitate three times by decantation with 1.5 *N* NH_4OH (concentrated NH_4OH, *d* 0.90, diluted with nine times as much water), and transfer the precipitate to the crucible. Use a rubber policeman to remove the precipitate from the sides of the glass beaker. Wash the precipitate with the 1.5 *N* NH_4OH until the filtrate gives no test for chloride when made acid with nitric acid and treated with a few drops of silver nitrate solution. To collect filtrate for this test, place a test tube in the suction flask underneath the filter funnel. It is important that all the ammonium chloride should be washed out of the crucible before washing with alcohol and ether. Finally wash four times with 5-ml portions of alcohol, followed by four 5-ml portions of ether. Draw air through the crucible for 5 minutes, wipe off the outside of the crucible with a clean cloth, and weigh after it has remained in a desiccator 15 minutes. The precipitate contains 28.93 per cent of P_2O_5.

(b) **Weighing as $MgNH_4PO_4 \cdot H_2O$.** Proceed exactly as in (*a*) but omit the treatment with alcohol and ether. After preparing the Gooch crucible with a suitable asbestos mat, place it in a small covered beaker and allow it to remain in the drying oven at 100° for at least an hour. Cool 15 minutes in a desiccator, and weigh carefully. After filtering off and washing the magnesium ammonium phosphate precipitate with 1.5 N NH_4OH till free from chloride, place the crucible in a small covered beaker and allow it to remain an hour in the drying oven at 100°, but make sure that the oven does not exceed this temperature by more than one degree. The precipitate contains 45.69 per cent P_2O_5.

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[1] The "magnesia mixture" is prepared, according to Schmitz, by dissolving 55 g of $MgCl_2 \cdot 6H_2O$ and 105 g of ammonium chloride in water, adding a little hydrochloric acid, and diluting to a volume of 1 l. For 0.1 g of P_2O_5, use 6 ml of this solution.

The hexahydrate changes to the monohydrate at about 50°. While drying 1 hour at 100°, there is no appreciable decomposition of the monohydrate. If, however, the temperature is raised, or the precipitate is kept at this temperature for a long time, an appreciable decomposition takes place and there is a loss of some ammonia as well as water.

(c) **Weighing as $Mg_2P_2O_7$.** This is the classic method of weighing the precipitate, and the literature furnishes abundant proof of the fact that accurate results can be obtained. On the other hand, it is one of the hardest tasks that the beginner in analytical chemistry has to perform, because it is only by careful ignition that a pure, white residue can be obtained. If the precipitate is ignited too rapidly, a dark-colored ash is obtained. This is caused sometimes by incomplete combustion of the filter paper and sometimes by a reduction of the phosphate by the hot ammonia vapors that are being expelled. If the precipitation has taken place in the presence of sodium salts, sometimes a little sodium salt is absorbed by the precipitate and it melts during the ignition to form a coating which makes it difficult to burn all the carbon of the paper. Because of the difficulty involved and the fact that good results are possible, this determination as magnesium pyrophosphate furnishes good experience to the beginner.

$$2MgNH_4PO_4{\cdot}6H_2O \rightarrow 13H_2O + 2NH_3 + Mg_2P_2O_7$$

Use an ashless filter paper for filtering off the magnesium ammonium phosphate precipitate. After washing it with 1.5 N NH_4OH, exactly as described under (*a*), moisten it with a saturated solution of ammonium nitrate in 1.5 N ammonia, dry, ignite slowly and carefully, and weigh.

If the weight of the precipitate is p, then the corresponding weights of H_3PO_4 and P_2O_5 are

$$\frac{2H_3PO_4 . p}{Mg_2P_2O_7} = \text{weight } H_3PO_4 \quad \text{and} \quad \frac{P_2O_5 . p}{Mg_2P_2O_7} = \text{weight } P_2O_5$$

The conversion of magnesium ammonium phosphate to magnesium pyrophosphate can also take place in a Gooch crucible. The crucible and its asbestos mat should be heated to about 800° and cooled in a desiccator before weighing it. After transferring the precipitate to the crucible and washing out all soluble salts, it should be dried at about 100° and then heated to about 800° for at least 15 minutes. If a muffle furnace is available this offers no difficulty. If the heating takes place over a free flame, a piece of platinum foil or the lid of a platinum crucible should be placed underneath the crucible so that the flame does not come into direct contact with the precipitate.

Analysis of Limestone or of Portland Cement

Portland cement is made by heating limestone with a clay rich in silica. The cement, therefore, contains the non-volatile constituents of both materials. It represents a silicate completely decomposable by dilute mineral acid. In the analysis of limestone, not much decomposable silicate is likely to be present, and the three important determinations are: lime, CaO; magnesia, MgO; and carbon dioxide, CO_2. In a commercial analysis, the residue insoluble in dilute acid is often weighed and called " insoluble material "; the precipitate obtained with ammonium hydroxide is ignited and weighed as " combined oxides " consisting chiefly of Fe_2O_3 and Al_2O_3. In the analysis of portland cement the procedure is similar except that special care is necessary for the determination of the silica, the iron is usually determined, the corresponding weight of Fe_2O_3 is deducted from the ignited ammonium hydroxide precipitate, and the difference is called alumina. This precipitate may also contain a little manganese, titanium, and traces of silica and phosphoric anhydride. With portland cement, the determination of carbon dioxide is unimportant but sulfate is usually determined because a little gypsum is commonly used in the preparation of the cement, but the calcium sulfate content should be kept low and specifications are rigid with respect to this point. The testing of portland cement also includes certain physical tests in addition to the chemical analysis which alone concerns us here.

The American Society for Testing Materials has adopted a standard set of specifications [1] for portland cement, including its physical and chemical testing. The chemical methods recommended were those formulated by a committee who made a special study of this analysis. The following directions are based upon the report of the committee, but the procedure has been modified slightly in minor details and no attempt is made to reproduce the same wording. This scheme of analysis is given partly because of the technical importance of portland cement and partly because it has proved a satisfactory procedure to place in the hands of students as representative of a complete analysis.

The mode of procedure adopted by the above-mentioned committee called for two evaporations for the removal of the silica. In the discussion of the method, however, it was pointed out that, by heating the residue at 120°, not correcting for impurities by the hydrofluoric acid treatment and not correcting the subsequent precipitate formed by ammonia for small traces of silica, results are obtained which are within the permissible analytical error of the correct values. In fact, by this more rapid method, a compensation of errors takes place and the results are often better than if the same operator attempted to carry out the analysis with the utmost precision possible.

The committee also recommended the use of platinum dishes and platinum crucibles as far as possible. The advantages gained are obvious, but the price of platinum has become so high that it is the duty of every practical chemist to avoid the use of platinum utensils wherever possible. The errors introduced by using porcelain instead of platinum are insignificant in most cases, although greater care must be taken to allow crucibles to cool before placing them in desiccators, and a longer time should elapse before weighing.

The original directions call for two precipitations of the calcium and for two precipitations of magnesium. This is unessential in the commercial testing of portland cement provided that the conditions recommended are carefully fulfilled. The directions apply equally well to the analysis of limestone.

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[1] *Proc. Am. Soc. Testing Materials,* **12**, 301–28 (1912).

Procedure. Weigh accurately to the nearest 0.1 mg about 0.5 g of limestone or cement into a 250-ml porcelain casserole, cover with 40 ml of water, and add 20 ml of 6 *N* hydrochloric acid (*d* 1.1), breaking up with a stirring rod any lumps that form. Cover the casserole with a watch glass and digest about 15 minutes on a hot plate until the cement is decomposed completely. Rinse off the bottom of the cover glass with a little water and evaporate to dryness on the water bath.[1] During the evaporation have the cover glass raised above the top of the casserole by means of a glass support. Heat the casserole and dry the residue in a hot closet at 120°.

Silica. Moisten the residue with 10 ml of 6 *N* hydrochloric acid, warm slightly, and add 150 ml of water. Cover the casserole with a watch glass and digest 10 minutes at a temperature near the boiling point. Filter into a 300-ml beaker; wash twice with 2 *N* hydrochloric acid and then with hot water till free from chloride. Transfer the moist precipitate, and filter to a weighed porcelain crucible with the paper folded so that the precipitate is entirely covered.[2] Smoke off the filter paper at a low heat without letting the paper take fire (cf. p. 181). Finally ignite at the full heat of the Méker burner until a constant weight is obtained of a perfectly white precipitate. Report as " insoluble residue " in the analysis of limestone or as " silica " in the analysis of portland cement.

Precipitation of Iron and Aluminum. To the filtrate and washings add ammonia solution until a slight ammoniacal odor persists after blowing away the vapors. Heat again just to boiling, and promptly filter off the precipitate of $Fe(OH)_3$ and $Al(OH)_3$. Wash the precipitate 6 times with small portions of hot water. Reserve the filtrate for the calcium and magnesium determinations.

Sometimes the precipitate contains a little calcium carbonate from the carbon dioxide in the air and often a little magnesium hydroxide. Wash the precipitate back into the casserole, place the casserole under the funnel, pour 5 ml of hot 3 *N* hydrochloric acid on the upper edge of the filter, and wash the filter with a little hot water. Continue the treatment with acid and water until all the precipitate left on the filter is dissolved. Finally wash the filter with a little dilute ammonia.

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[1] At this temperature, the silica acid becomes dehydrated so that it is practically insoluble in dilute acids. The presence of the calcium chloride from the cement helps the dehydration. The quantity of silica that passes into the filtrate is negligible and more than balanced by that obtained from the reagents and dishes. The residue should not be baked too hard. At higher temperatures, combination of basic magnesium salt and silicic acid takes place and alumina is made very insoluble.

[2] Dry silica is very pulverulent and easily lost if the gases from the paper escape too violently, as when it takes fire.

Precipitate with ammonia just as before, filter through the original filter, and wash this second precipitate till free from chloride. Ignite the second precipitate wet in a porcelain crucible and weigh as Fe_2O_3 + Al_2O_3, neglecting the small quantities of TiO_2, P_2O_5, and Mn_3O_4 which it may possibly contain. Unite the filtrate with that obtained from the first precipitate.

In the analysis of limestone, the weight of this precipitate will usually be small. The iron content will often arise from a little ferrous carbonate present in the sample. Disregard this fact and simply report the percentage of " combined oxides " present.

In the analysis of portland cement, the precipitate after ignition should be largely Al_2O_3, and it is customary to regard it as Al_2O_3 + a little Fe_2O_3. The quantity of the ferric oxide should be determined by titration, as follows:

Ferric Oxide. Transfer the ignited precipitate to a small beaker. Dissolve the traces that remain adhering to the crucible by heating small portions of 6 *N* hydrochloric acid in it, finally pouring each portion into the beaker. Use 20 ml of acid in all. Do not at any time dilute the hydrochloric acid until all the iron in the beaker is dissolved. Heat the acid with the iron and aluminum oxides at about 90° until all the iron has dissolved (cf. p. 104). When a clear solution is obtained, place the beaker on a filter, reduce carefully with stannous chloride, and determine the iron content by the Zimmermann-Reinhardt process. Compute the percentage of Fe_2O_3 present, and subtract this from the above weight of the oxides to get the percentage of Al_2O_3.

Calcium Oxide. Make the combined filtrates acid with acetic acid, bring to a volume of about 400 ml, heat to 80–90°, and slowly add, while stirring, 30 ml of hot 0.5 *N* ammonium oxalate solution. Slowly add ammonium hydroxide until the solution is slightly ammonical, and allow the precipitate to stand an hour, but not much longer, before filtering.

If considerable magnesium is present in the solution, some magnesium oxalate will come down with the calcium oxalate. If, therefore, more than 10 per cent of MgO is present in the substance analyzed, it is best to redissolve the calcium oxalate precipitate and repeat the precipitation, using a paper filter for filtering off the precipitate. When all the solution has passed through the filter, wash the precipitate with about 15 ml of hot water. Then rinse the precipitate back into the original beaker by holding the funnel in an inverted position and directing a stream of hot water against it. Replace the funnel in the support and wash the filter with about 25 ml of hot 3 *N* hydrochloric acid. Heat the acid in a test tube, pour it upon the upper edge of the paper, and catch the liquid as it runs through the filter in the beaker containing the precipitate. Finally wash the filter with a little hot water (and with dilute ammonia if it is to be used again for filtering the next precipitate). Heat the dilute acid in the beaker and add a little more acid if necessary to dissolve the precipitate completely. Dilute the solution to about 250 ml and repeat the precipitation of the oxalate at the boiling temperature, adding ammonia and 5 ml more of the ammonium oxalate reagent. Since the solution already contains oxalic acid equivalent to the calcium, only a little more reagent is necessary.

The calcium content of the precipitated calcium oxalate can be determined in various ways, all of which give good results.

1. The filtered precipitate corresponds to the formula $CaC_2O_4 \cdot H_2O$. It can be weighed in this form without difficulty because the water of crystallization is retained even after long heating at temperatures slightly above the boiling point of water.

2. It can be weighed as anhydrous calcium oxalate. To accomplish this it has been recommended that the precipitate be heated at 200–300° for some time.

3. It can be converted to calcium carbonate by heating to dull redness. The reaction

$$CaC_2O_4 \rightarrow CaCO_3 + CO$$

takes place at about 400°, but Foote and Bradley[1] have shown that it is safe to heat at 675–800° if the precipitate is in a tubulated crucible and a current of CO_2 is constantly led through the crucible while it is being heated. The common way of accomplishing the decomposition is to heat for some time to dull redness, cool, moisten with a little ammonium carbonate reagent, and again heat carefully until no more odor of ammonia is preceptible. For the first heating, 2 hours in a muffle at 500° has been recommended, and, after the treatment with ammonium carbonate solution, drying at 110° is sufficient.

4. After the ignition to calcium carbonate (and it does no harm if some calcium oxide is formed), the precipitate can be dissolved in a measured volume of 0.5 *N* hydrochloric acid and the excess acid titrated with 0.5 *N* sodium hydroxide to a methyl orange end point.

5. By strong ignition, calcium carbonate is changed to calcium oxide, which can be weighed. This method of handling the calcium oxalate precipitate is generally regarded as the best. Quantitative conversion can be accomplished in a covered platinum crucible by heating 1 hour with the full heat of a good Tirrill burner. The crucible should be covered loosely to prevent unnecessary loss of heat. A much shorter period of heating is necessary over a Méker burner or the blast lamp. A muffle heated to about 1000° can be used to advantage. The conversion of calcium oxalate to calcium oxide cannot be accomplished by heating in an open *porcelain* crucible over a Bunsen burner, and it requires a very long time to accomplish the conversion by heating in a covered porcelain crucible over a large Méker burner. The determination as oxide, therefore, is not to be recommended unless a muffle furnace or a platinum crucible is available.

6. The original calcium oxalate precipitate can be dissolved in dilute acid and the liberated oxalic acid titrated with potassium permanganate solution. This is one of the most popular methods and gives good results. For this method of analysis, the precipitate should not contain over 0.1 g of calcium. In portland cement

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[1] *J. Am. Chem. Soc.*, **48**, 676 (1926).

analysis, therefore, an aliquot of the filtrate from the iron and alumina precipitation should be taken or an aliquot of the solution of the calcium oxalate precipitate in acid. To take an aliquot of any solution, dilute it to a definite volume in a volumetric measuring-flask. After diluting to the mark, mix the solution by pouring it back and forth at least four times, using a beaker which is clean and dry at the start. Then, by means of a pipet or a smaller measuring-flask take out at once one or more fractional parts of the entire solution for further analysis. Thus the filtrate from the ammonia precipitation can be diluted to exactly 500 ml, the solution mixed and 50 ml (= one-tenth) taken for the calcium determination. The word *aliquot* in mathematics designates a number that will divide a larger number without leaving a remainder. In analytical chemistry it is used to represent an exact simple fraction of the whole sample taken for analysis.

Weighing as $CaC_2O_4 \cdot H_2O$. Use a weighed Gooch crucible for collecting the calcium oxalate precipitate. Wash the precipitate with hot 0.25 per cent ammonium oxalate solution until 3 ml of the washings gives no test for chloride on adding HNO_3 to an acid reaction and a few drops of $AgNO_3$ reagent. Then, with gentle suction, wash with six 5-ml portions of hot water, four 5-ml portions of ethyl alcohol, and four 5-ml portions of ether. Drain off each portion of wash liquid before adding more. Finally draw air through the washed precipitate for 5 minutes; wipe off the outside of the crucible and allow it to remain in a desiccator 15 minutes before weighing. The originally empty crucible should be washed, dried, and weighed in exactly the same way. The precipitate contains 38.39 per cent CaO. Save the filtrate for the determination of magnesium, preferably *without* the alcohol and ether washings.

Weighing as CaO. Use an ashless paper for collecting the precipitate. Wash the precipitate with hot water until free from chloride, and save the filtrate for the magnesium determination. Transfer the precipitate to a weighed *platinum* crucible. Ignite carefully with the flame at the mouth of the crucible until the precipitate is dry, and then heat with a small flame at the base of the crucible until all the paper is decomposed without letting it take fire. Then gradually raise the temperature and heat over a Tirrill burner for an hour with the crucible in an upright position and covered. Cool to about 100°, place in a desiccator, and weigh after 15 minutes. Repeat the heating until after cooling a constant weight is obtained. The calcium oxide is somewhat hygroscopic but is not difficult to weigh if it has been washed free from chloride. Call the weight constant if it agrees within 0.2 mg with the previous weight.

Titration with Permanganate. Either a paper filter or a Gooch crucible can be used. After the precipitate has been washed free from chloride, transfer the precipitate together with the filter to a 400-ml beaker and dissolve the precipitate in 100-ml of warm 3 N sulfuric acid. Titrate at 70° with potassium permanganate as described in Chapter VI for the standardization of permanganate against sodium oxalate.

Magnesium Oxide. Make sure that the precipitation of $CaC_2O_4 \cdot H_2O$ was complete by adding 5 ml more of ammonium oxalate reagent.

At this stage, the solution will contain considerable ammonium salt. Ammonium salt is necessary to prevent the precipitation of $Mg(OH)_2$ with the hydroxides of iron and aluminum, and it also helps to prevent precipitation of MgC_2O_4. If the above procedure has been followed closely and only one precipitation of calcium oxalate made, which is permissible when the magnesium content is low, the magnesium can be precipitated as $MgNH_4PO_4 \cdot 6H_2O$ without removal of ammonium salts. It then is merely necessary to make the filtrate from the calcium oxalate precipitation acid with HCl, concentrate to about 300 ml by heating on the hot plate at a temperature somewhat below the boiling point, and precipitate with $(NH_4)_2HPO_4$ as will be described. If the solution should accidentally be evaporated to dryness, moisten the residue with strong HCl (to dissolve MgC_2O_4 or a basic salt), dilute to dissolve the ammonium salts, heat to boiling, and filter. Filtration is necessary because some silica is always present either from the reagents or from the action of the reagents on the beakers used.

Ammonium salts in small quantities are desirable in precipitating magnesium, but when considerable oxalate or ammonium chloride is present it will prevent precipitation of quite appreciable quantities of $MgNH_4PO_4 \cdot 6H_2O$. For that reason, magnesium is often missed in qualitative analysis, and it is quite common for chemists to report too low values for magnesium. It is safest always to remove excess ammonium salts by evaporating with nitric acid; the ammonium ion is oxidized to nitrogen gas. It is well to remember that approximately 6 N HCl and 15 N HNO_3 are constant-boiling acids, and approximately these concentrations are obtained when dilute solutions of these acids are evaporated.

Procedure. Add 75 ml of concentrated HNO_3 to the combined filtrates and washings from the $CaC_2O_4 \cdot H_2O$ precipitation, and evaporate to dryness on the steam bath or hot plate. Do not boil the solution or there will be loss by spattering. Keep the beaker covered with a watch glass supported above the upper rim of the beaker. A *glass* triangle, or glass supports which are made for this purpose, should be used to support the watch glass. To the small residue obtained, add 2 ml of concentrated HCl and 25 ml of water. Heat nearly to boiling, and, after a few minutes, filter off the silica residue through a small filter. Wash the beaker, and filter thoroughly with hot water. The silica comes from the action of reagents on reagent bottles or on the beakers used in the analysis.

Dilute the solution to about 150 ml; add about 1.2 g of $(NH_4)_2HPO_4$ dissolved in a little water and a few drops of phenolphthalein indicator solution. Heat nearly to the boiling point, and then slowly add 1.5 N ammonia water until a faint pink color is obtained and a slight precipitation takes place. Stir well for about a minute, touching the sides of the beaker as little as possible. When the precipitate has become distinctly crystalline, add more ammonia until a deep color is obtained with the phenolphthalein. Allow the solution to cool, then add one-fifth the solution's volume of concentrated ammonium hydroxide and allow to stand over night.

Sometimes, when considerable ammonium salt is present, no precipitation takes place on the addition of the ammonia, but usually the precipitate will appear after standing over night in the presence of 2.5 N NH_4OH, which is the approximate concentration obtained by following the above directions. Besides the above treatment, three other methods can be recommended for removing ammonium salts. (1) Evaporate the solution to dryness in a porcelain casserole, and heat the dry residue until no more vapors of ammonium salt are evolved. Cool, moisten the residue with 5 ml of 6 N hydrochloric acid, heat till basic salts are dissolved, dilute to about 25 ml, filter and wash the filter with hot water until free from chloride. Add 5 ml of concentrated hydrochloric acid and some alkali phosphate if not already present. Dilute the solution to about 125 ml, heat nearly to boiling, and neutralize with ammonia as directed above. (2) Evaporate the solution to dryness after adding some nitric acid. To the residue add 25 ml of water, 50 ml of concentrated nitric acid, and 15 ml of concentrated hydrochloric acid, and again evaporate to dryness. By this treatment with aqua regia, ammonium salts are oxidized to nitrogen. Finally treat this residue with 5 ml of 6 N HCl and 20 ml of water. Heat for a few minutes to dissolve basic salts and filter into a 250-ml beaker. Wash the filter with hot water till free from chloride, add 5 ml of concentrated hydrochloric acid, dilute to 125 ml, add 1.2 g of diammonium phosphate, and precipitate with ammonia as described above. (3) To the neutral solution add 5 g of sodium acetate and an excess of bromine water. Heat carefully, and add more bromine until finally all the ammonium salt is oxidized. The reaction

$$2NH_4^+ + 3Br_2 + 8C_2H_3O_2^- \rightarrow N_2 + 6Br^- + 8HC_2H_3O_2$$

will take place provided that sufficient sodium acetate anion is present to keep the solution buffered.

The precipitate of ammonium magnesium phosphate, $NH_4MgPO_4\cdot 6H_2O$, is the same as that obtained in the analysis of apatite, where it was formed from the phosphate present. Filter, wash, and weigh by any one of the methods described on pp. 205–206.

Formerly it was common practice to precipitate magnesium ammonium phosphate in the cold. Neubauer[1] showed, however, that this sometimes leads to high results and at other times the results are low. They are low when the precipitation takes place in strongly ammoniacal solutions containing but little ammonium salts, particularly when the phosphate solution is added slowly. Tribasic magnesium phosphate, $Mg_3(PO_4)_2$, contaminates the precipitate. On the other hand, the results are too high if the precipitation takes place in neutral or slightly ammoniacal solution in the presence of considerable ammonium salts. In this case more or less monomagnesium ammonium phosphate, $Mg(NH_4)_4(PO_4)_2$, is formed. This compound is changed to magnesium metaphosphate by gentle ignition

$$2Mg(NH_4)_4(PO_4)_2 = 2Mg(PO_3)_2 + 8NH_3 + 4H_2O$$

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[1] *Z. angew Chem.*, **1896**, 439. See also Gooch and Austin, *Z. anorg. Chem.* **20**, 121.

and the results are too high. When only a little of the metaphosphate is present, the temperature of the blast lamp will eventually lead to volatilization of some phosphorus pentoxide, so that nearly correct results are then obtained.

$$2Mg(PO_3)_2 = Mg_2P_2O_7 + P_2O_5$$

Recent studies have shown that during the ignition of $MgNH_4PO_4$ there is likely to be a loss of phosphorus due to the reduction by hot carbon. Two ways of overcoming this difficulty have been suggested. McNabb[1] recommends dissolving the precipitate off the filter by means of nitric acid, making the solution slightly ammoniacal, and evaporating in a weighed porcelain crucible. McCandless and Burton[2] recommend washing the precipitate at the last with a concentrated solution of ammonium nitrate in 1.5 N ammonium hydroxide. In either case careful ignition gives a white precipitate of magnesium pyrophosphate and there is no reduction and loss of phosphorus. Schmitz[3] has shown that precipitation in the presence of ammonium acetate is advantageous.

The separation of calcium from magnesium depends upon the different solubilities of the two oxalates. Less than 0.2 mg of $CaC_2O_4 \cdot H_2O$ is dissolved by 1 *liter* of hot, 0.25 per cent ammonium oxalate solution, but the same quantity of hot water will dissolve 1 g of $MgC_2O_4 \cdot 2H_2O$. Twenty grams of $(NH_4)_2C_2O_4 \cdot H_2O$ will not interfere with the complete precipitation of calcium but, even in the presence of calcium, will prevent precipitation of Mg^{++} when as much as 2.7 g of $MgCl_2 \cdot 6H_2O$ is present in 100 ml of solution.[4]

It has been known for a long time that, when calcium oxalate is precipitated in the presence of magnesium ions, particularly when the solution has remained for a long time in contact with the precipitate, some magnesium is likely to be found in the precipitate. This has been attributed to the formation of a solid solution of magnesium oxalate in calcium oxalate, to adsorption or occlusion of magnesium oxalate,[5] or to the gradual breaking down of a supersaturated solution of magnesium oxalate.[6] For this reason it is quite generally believed that a precipitate of calcium oxalate formed in the presence of magnesium ions is rarely, if ever, pure,[7] and therefore it is customary to filter off the precipitate, redissolve it in acid, and reprecipitate whenever the content of magnesium amounts to more than a few milligrams. Bach and W. Fresenius,[8] however, have apparently proved that Richards[9] was right in asserting that the separation is accurate if the proper conditions are maintained.

For the precipitation of small quantities of calcium in the presence of much magnesium, three methods have been proposed. (1) The calcium oxalate is formed in the usual way; the precipitate is filtered off, dissolved, and reprecipitated a second and a third time. (2) The calcium oxalate is precipitated in the presence of ammonium salt using only a slight excess of ammonium oxalate over that required by the calcium. (3) The calcium oxalate is precipitated in 100 ml of solution by the addition of 20 g of ammonium oxalate; the hot solution is filtered off after standing a short time, and no attention is paid to any precipitate of magnesium oxalate that forms in the cold filtrate after some time. When the last method is used, the excess ammonium salts must be removed before attempting to precipitate $MgNH_4PO_4$.

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[1] *J. Am. Chem. Soc.*, **49**, 891, 1451 (1927).

[2] *Ind. Eng. Chem.*, **16**, 1267 (1924).

[3] *Z. anal. Chem.*, **65**, 46–53 (1924) cf. McNabb, *J. Am. Chem. Soc.*, **50**, 300 (1928).

[4] Bobtelsky and Malkowa-Janowski, *Z. angew Chem.*, **40**, 1437 (1927).

[5] T. W. Richards, *Z. anorg. Chem.*, **28**, 701 (1901).

[6] W. M. Fischer, *Z. anal. Chem.*, **153**, 62 (1926).

[7] Cf. Lundell and Knowles, *J. Am. Ceramic Soc.*, **10**, 834 (1927).

[8] *Chem. Ztg.*, **49**, 514 (1926).

[9] *Loc. cit.*

Determination of Carbon Dioxide

The apparatus for this determination is shown in Fig. 31. The decomposition flask *F* should have a capacity of about 250 ml; a wide-mouthed flask such as used for Soxhlet extractions is also suitable. The tube *T* of 8-mm diameter and about 30 cm long acts as an efficient air condenser. If a hole is blown at *E*, the flow of gas from the decomposition flask is not impeded by condensed moisture during the experiment, but this is not very important.

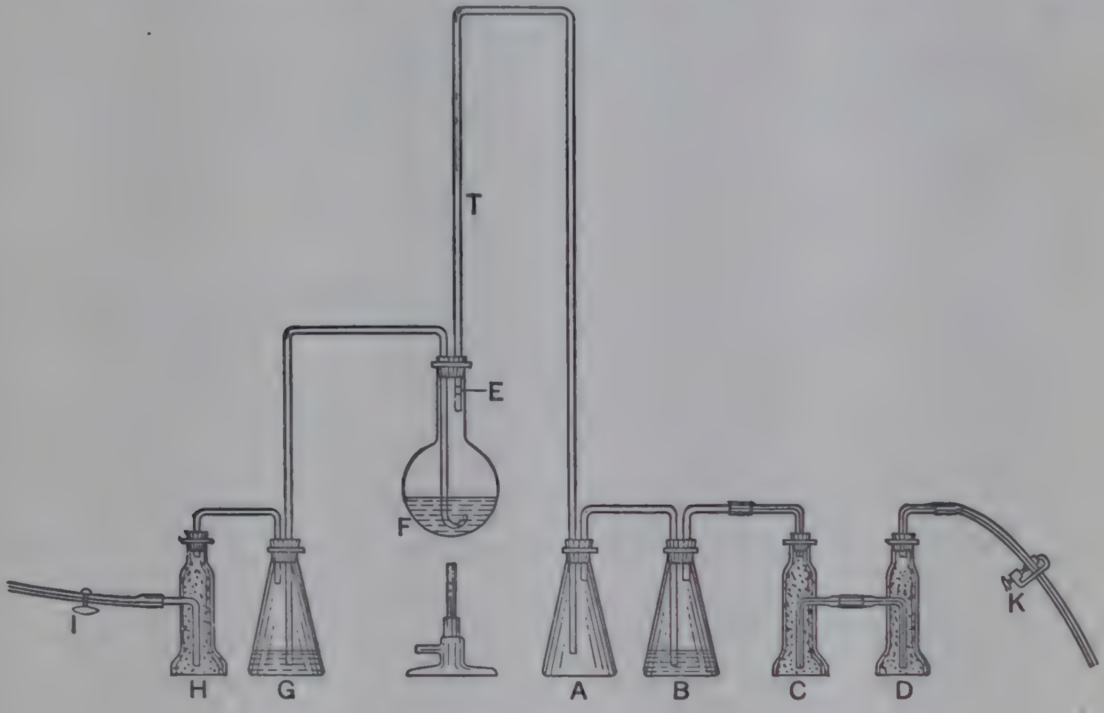

FIG. 31.

A and *B* are Erlenmeyer flasks of 100- to 125-ml capacity. *A* is empty, but *B* contains enough concentrated sulfuric acid to act as a bubble counter and to show whether the apparatus is tight. *C* is a Midvale absorption tube containing some drying agent such as *Dehydrite*, $Mg(ClO_4)_2 \cdot 3H_2O$, between cotton plugs, and *D* is a similar tube containing Ascarite (asbestos impregnated with NaOH) with cotton at the top and bottom. Instead of *Dehydrite*, calcium chloride (of the grade marked "for drying tubes"), *Anhydrone*, $Mg(ClO_4)_2$ or *Desicclora*, $Ba(ClO_4)_2$, can be used. The tube H should contain Ascarite to remove CO_2 from the air.

By means of *K*, a small screw clamp on rubber tubing which is connected with suction, the rate of flow of gas through the apparatus can be regulated. *G* is another 100- to 125-ml Erlenmeyer flask which is, at the start, about half full of normal HCl. *H* contains Ascarite. In the drawing a Midvale tube is shown at *H*, but a U-tube or any absorbing tower can be used equally well. The glass tubing that connects *F* and *G* should reach nearly to the bottom of each flask; it is well to make the tube a little narrower where it ends at the bottom of the flask *F* and to have the tip turned upward.

For decomposing the carbonate, sulfuric acid, hydrochloric acid, phosphoric acid, perchloric acid, and chromic acid have all been recommended. In the analysis of baking-powders, no acid is required because water alone causes the decomposition; therefore the flask *F* must be perfectly dry at the start.

If the substance contains besides the carbonate a sulfide which is decomposable with acid, introduce before *A* and *B* a tube containing pumice impregnated with copper sulfate.[1] This serves to absorb all the hydrogen sulfide evolved.

Procedure. First make sure that the apparatus is tight. Have the flask *G* empty, but pour enough water in the flask *F* to seal the end of the tubing. Close the pinchcock *I* on the rubber tubing at the extreme left of the apparatus so that air cannot enter there, and make sure that all the rubber stoppers are inserted tightly in the necks of the four flasks. Open the screw clamp *K* a little and apply gentle suction so that at first about 2 bubbles of air per second will pass through the liquid in *B*. If the apparatus is tight the current of air will soon slow down. When the air is passing at the rate of about 1 bubble in 2 seconds, close *K* tightly and take the rubber tubing off the suction pipe. There should now be no movement of air through the liquids in *F* or *B*. After a few minutes, carefully allow air to enter the apparatus through the tubing at *I* by squeezing the end of the tubing to the left of *I* between the thumb and finger and alternately releasing the pressure at *I* and between the fingers. If the apparatus is tight, about as many bubbles of air will flow through the apparatus as were withdrawn during the evacuation.

During this testing, the tube *D*, which has been wiped dry with a clean linen cloth, should be resting in the balance case. After it has been there at least 10 minutes, remove the rubber tubing from the ends of the capillary tubing and weigh it and its contents to 0.1 mg. Weigh accurately 0.5–0.6 g of carbonate into the dry flask *F*, and add enough water to seal the end of the tubing at the bottom of the flask. Connect the weighed Ascarite tube to the front end of the train, place about 50 ml of approximately *N* hydrochloric acid in the flask *G*, and make sure that the pinchcock *I* is open. Apply gentle suction, and regulate the screw clamp *K* so that about 2 bubbles of gas per second pass through the sulfuric acid in *B*. When all the acid has been drawn from *G* into the flask *F*, start heating the contents of *F*. During the heating, watch the glass tubing that connects the flasks *F* and *G* and do not let the liquid pass from *F* toward *G*, as will happen if the liquid in *F* is heated too rapidly. If the liquid starts going toward *G*, turn down the flame and, if necessary, increase the suction. Finally boil the liquid in *F* for 1 minute. Then take away the flame and continue drawing air through the apparatus, at the rate of 2–3 bubbles per second, for 20 minutes longer, in order to get all the CO_2 into the absorption tube *D*. After this, detach *D* from the train and connect the two open ends with a piece of rubber tubing, to prevent absorption of CO_2 from the air. Wipe the tube carefully with a piece of clean linen and allow it to stand in the balance case for 15 minutes. Remove the rubber tubing and weigh. The gain in weight represents absorbed CO_2.

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[1] Cover 60 g of pumice pieces in a porcelain dish with a concentrated solution of 30–35 g of copper sulfate. Evaporate the solution to dryness with constant stirring, and heat the residue at 150–160° for 4–5 hours.

Remark. The results obtained by this method are perfectly satisfactory. For the analysis of substances containing small amounts of carbonate, take 3–10 g for the analysis. It is convenient to use another Midvale tube as a tare when weighing the tube *D*, then recording merely the difference in weight. Sulfites interfere with this determination, but the difficulty can be overcome by decomposing the carbonate with an excess of potassium dichromate solution and adding the dilute acid later.[1]

HOME PROBLEMS

106. If a sample of apatite corresponds exactly to the formula $[Ca_3(PO_4)_2]_3 \cdot CaFCl$ (mol. wt. = 1025), compute for a sample weighing 0.15 g: (*a*) the volume of acid $(NH_4)_2MoO_4$ solution (cf. p. 249) theoretically required to react with it; (*b*) the volume of 0.5 *N* NaOH required to dissolve the yellow precipitate and leave the solution neutral to phenolphthalein (cf. p. 252); (*c*) the volume of ferric alum solution containing 0.01 g Fe per ml) required to react with the molybdenum solution after it had been reduced to the trivalent condition, assuming that half the Mo is oxidized to the valence of 4 and half to the valence of 5; (*d*) the volume of " magnesia mixture " (cf. p. 205) required to precipitate the P as magnesium ammonium phosphate; and (*e*) the weight of magnesium pyrophosphate which could be obtained from this sample.

107. From 0.674 g of a mixture containing only $MgCO_3$ and $BaCO_3$ there was obtained 0.3117 g of CO_2. Compute the percentages of MgO and of BaO in the mixture.

108. The calcium in 0.9380 g of limestone is precipitated as CaC_2O_4 and weighed as CaO. If the weight of the CaO is 0.2606 g, compute the volume of gas evolved during ignition, measured wet at 20° C and 765 mm pressure. Neglect the solubility of CO and CO_2 in water, and assume that the gram-molecular volume of each gas is 22.4 l under standard conditions.

109. If a sample of dry limestone contains 93.0 per cent of $CaCO_3$, 5.16 per cent of $MgCO_3$, and 1.84 per cent of SiO_2, calculate the weight of " lime " obtained by calcining 3 tons of limestone and the percentages of CaO and MgO in the " lime " if it contains no CO_2 nor moisture. (The word " lime " in this problem and in Problem 111 signifies the weight of the non-volatile constituents of the limestone. Note that the original percentages are based on the weight of the limestone and the final percentages refer to the weight of the non-volatile residue.)

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[1] E. R. Marle, *J. Chem. Soc.*, **95**, 1491 (1909). If it is desired to determine a small quantity of carbon dioxide in a gas containing considerable hydrochloric acid and hydrogen sulfide, use a tube containing finely divided metallic copper, instead of the pumice and copper sulfate, to absorb the hydrogen sulfide, and a tube containing *p*-nitrosodimethylaniline to absorb hydrochloric acid, Vernon and Whitby, *J. Soc. Chem. Ind.*, **47**, 257 (1928).

110. What weight of limestone should be taken for analysis so that the number of milliliters of CO_2 evolved on treatment with acid (measured dry at 18° and 763 mm pressure) will be the same as the percentage of CO_2 present?

111. Lime is to be made by heating a sample of dolomite containing 96.46 per cent of carbonates of calcium and magnesium, 2.21 per cent of SiO_2, 1.33 per cent of H_2O, and 10.23 per cent of MgO as carbonate. The product obtained by calcination contained all the CaO, MgO, and SiO_2 originally present with only 1.37 per cent of CO_2. Calculate the percentages of CaO and MgO in the calcined lime.

112. A sample of limestone containing 34.75 per cent of Ca was analyzed by a student, using a 1-g sample, and the value 35.26 per cent of Ca was reported. On the assumption that the error was due to the presence of a little $CaCO_3$ in the ignited calcium precipitate which the student assumed to be pure CaO, find the percentage of $CaCO_3$ in the ignited product. What volume of sulfuric acid (*d* 1.06) containing 8.77 per cent of H_2SO_4 by weight should be added to the product in order to convert it to sulfate?

113. If the precipitate of $CaC_2O_4 \cdot H_2O$ obtained from 0.5 g portland cement with 63 per cent CaO is dissolved in dilute acid and titrated with $KMnO_4$, how many milliliters will be required of 0.12 *N* solution?

114. If the precipitate of $CaC_2O_4 \cdot H_2O$ from 0.5 g of portland cement with 63 per cent CaO is heated until all the oxalate is decomposed into $CaCO_3$ (and perhaps some CaO) how many milliliters of 0.12 *N* HCl will be necessary to dissolve the residue?

115. An excellent method for determining magnesium consists in precipitation with 8-hydroxyquinoline. The precipitate of $Mg(C_9H_6ON)_2$ can be dried at 135° and weighed or it can be dissolved in dilute HCl and brominated by treatment with $KBrO_3$ and KBr. The excess bromine can be determined iodimetrically by adding excess KI and titrating with $Na_2S_2O_3$ solution. Calculate the per cent MgO in a mineral if the precipitate of magnesium hydroxyquinolate is dissolved in acid, treated with 25.00 ml of 0.2 *N* $KBrO_3$-KBr solution, and then, after the addition of KI, the excess bromine liberates iodine equivalent to 5.00 ml of 0.12 *N* $Na_2S_2O_3$ solution. The reactions are as follows:

$$\begin{gathered}
Mg(C_9H_6ON)_2 + 2H^+ \rightarrow Mg^{++} + 2C_9H_7ON \\
2C_9H_7ON + 4Br_2 \rightarrow 2C_9H_5Br_2ON + 4HBr \\
BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \\
Br_2 + 2I^- \rightarrow 2Br^- + I_2 \\
I_2 + S_2O_3^{--} \rightarrow S_4O_6^{--} + 2I^-
\end{gathered}$$

CHAPTER XIII

THEORY OF ELECTROLYSIS. ANALYSIS OF BRASS

In electrolytic analysis, the substance to be weighed at the end of the experiment is deposited upon one of the electrodes by the passage of an electric current through the solution which is being analyzed. Usually a metallic deposit is obtained upon the negative electrode, or cathode, but sometimes an oxide deposit of an element such as lead, manganese, uranium, or molybdenum can be obtained upon the positive electrode, or anode. Just as in gravimetric analysis it is necessary to know something about the theory of solutions with respect to precipitation in order to be able to work out intelligently the best conditions for obtaining pure precipitates and complete precipitation, so in electrolytic work it is desirable to know how the electric current behaves toward solutions, and the effect of different strengths and of different voltages. It is necessary to know what happens when an electric current is passed through a solution.

If the wires from the positive and negative poles of a suitable source of current are each connected with separate pieces of platinum wire or foil and suspended a little distance apart in a sugar solution or in chloroform, it will be found that the sugar solution or the chloroform is a very poor conductor. If, however, the pieces of platinum, called *electrodes* when they are used in this way, are suspended in dilute sulfuric acid, in dilute sodium hydroxide solution, or in a solution of sodium chloride, these liquids will be found to be much better conductors of electricity, as would be shown by placing an ammeter in the circuit. On the basis of their behavior toward the electric current, the solutions of all soluble substances can be divided into two classes: those which conduct electricity well and those which do not. Substances which in aqueous solution conduct electricity are called *electrolytes.* To this class belong most acids, most bases, and nearly all salts; it is with these that electrolytic analysis is concerned.

Faraday, who, at the beginning of the nineteenth century, was the first to give the names *anode* and *cathode* to the electrodes,[1] noticed that the components of the electrolyte migrated toward one or the other of the electrodes and called these components *ions* (wanderers). The component which moves toward the anode he called the *anion*, and that which moves toward the cathode the *cation*. Faraday assumed that the electric current dissociated the substance into these ions, but we now know that the ions are already present in the solution and the conductivity of the solution is determined by (1) the number of ions present in the solution, (2) the electric charge which the ions bear, and (3) the rates at which the ions move through the solution. The passage of the current through the solution from one electrode to the other is a purely physical change involving merely the migration of the ions. When the electricity passes from the wire to the solution or from the solution to the other wire, a chemical change takes place, an *oxidation* at the anode and a *reduction* at the cathode. The two processes always take place simultaneously, and the oxidation at the anode is always equivalent to the reduction at the cathode. These oxidation and reduction reactions take place independently, and the conductivity of the solution may be due almost entirely to electrolytes present in the solution which take no part whatsoever in the chemical reactions at the electrodes.

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[1] It is true that in selecting these terms Faraday received considerable assistance from the eminent scholar, Rev. William Whewell, D.D. (1794–1886), whose aid Faraday had solicited in 1833. Faraday published the names in 1834.

Ohm's law:

$$\text{current strength } (\textit{amperes}) = \frac{\text{electromotive force } (\textit{volts})}{\text{resistance } (\textit{ohms})}$$

or

$$I = \frac{E}{R}$$

holds not only for the passage of electricity along a solid conductor (*conductor of the first class*) but also for the passage of electricity through the solution of an electrolyte (*conductor of the second class*).

The *ampere*, or unit of current strength, is the current which will deposit 1.118 mg of silver in 1 second from a solution containing about 15 g of pure silver nitrate in 85 ml of distilled water.

The *ohm*, or unit for measuring resistance, is the resistance offered at 0° C by a column of mercury 106.3 cm long weighing 14.4521 g and having a cross section of 1 sq mm.

The *volt*, or unit for measuring potential difference or electromotive force, is the force which produces a current of 1 ampere through a resistance of 1 ohm. When two of these three factors are known the third can be computed by Ohm's law.

The deposition of a metal like silver from a solution of a silver salt or, in other words, the reduction of silver ions to metallic silver depends upon the neutralization of the positive charges borne by the ions by the negative electricity from the electrode. In terms of the electron theory, the passage of electricity along a wire represents a flow of electrons, or units of negative electricity, in a direction opposite to the arrow that is used conventionally to express the positive to negative direction of the current. At the cathode, these electrons leave the wire and attach themselves to something present in the solution, causing a chemical reduction.

$$\mathrm{Ag}^+ + e \rightarrow \mathbf{Ag}$$

Faraday found that *the quantities of material deposited at the electrode in a unit of time are proportional to the current strengths used* and *the quantities of different substances deposited in equal lengths of time by the same current stand in the same relation to one another as their electrochemical equivalents.*

These electrochemical equivalents are oxidation and reduction equivalents. An atomic weight in grams of univalent metal ions like Ag^+ carries a charge such that it requires 96,500 coulombs (ampere-seconds) or 26.82 ampere-hours of electricity to deposit 1 atomic weight in grams of silver. The same quantity of electricity will cause the deposition of only ½ gram atom of copper from the solution of a cupric salt because the cupric ion is bivalent. Equations such as $\mathrm{Ag}^+ + e = \mathbf{Ag}$ and $\mathrm{Cu}^{++} + 2e = \mathbf{Cu}$ signify that 1 atom of silver requires 1 unit of negative electricity to change it from the ion to the metal and 1 atom of copper requires 2 units of negative electricity to change it from the ion to the free metal. The quantity of electricity represented by 96,500 coulombs bears the same relation to the quantity of electricity corresponding to the electron that the gram atom bears to the actual atom; it is estimated to be 6.06×10^{23} times as large. This enormously large figure is called *Avogadro's number* and represents the number of actual atoms in a gram-atom. The value 96,500 coulombs or, since there are 3600 seconds in an hour, 26.82 ampere-hours, is called the faraday and is often designated by the letter F. The quantity of metal ion reduced by 1 faraday of electricity is the electrochemical equivalent.[1] The equation $\mathrm{Cu}^{++} + 2F \rightarrow \mathbf{Cu}$ means that 2 faradays are required to change 1 mole of copper ions to metallic copper. In other words $1F = 6.06 \times 10^{23}e$.

It should be mentioned, here, that the computation of the quantities deposited in accordance with Faraday's law will give values corresponding to those obtained experimentally only if all the current is used for the discharge of the metal in question. This does not always happen, for during an electrolysis hydrogen gas is sometimes evolved before all the copper is deposited. The *current yield* or *current efficiency* is then less than 100 per cent with respect to the desired reaction.

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[1] Some authorities call the electrochemical equivalent the quantity deposited or reduced by 1 coulomb of electricity. It is more convenient to define the equivalent as the quantity deposited by 96,500 coulombs.

Two other units are of interest in connection with electrical measurements, the unit of *work* and the unit of *power*. The *joule* is the unit of work. It is equivalent to 10^7 ergs or to 1 watt-second. The unit of power used in commercial work is the watt (or the kilowatt which is 1000 watts), which represents work done at the rate of 1 joule per second. *Multiplying the volts by the amperage in any experiment gives watts, and multiplying this by the time in seconds gives watt-seconds or joules.*

Electrolytic analysis had met with remarkable success before the significance of the electromotive force or potential was recognized. The positively charged cations during electrolysis are attracted toward the negatively charged cathode, but when the ions get to the electrode the cathode potential has a great deal to do with respect to the chemical reaction that takes place. The *electrolytic solution pressure* of the metal has to be overcome.

When a substance like sugar lies as a solid at the bottom of a beaker filled with water, the molecules of sugar begin to distribute themselves in the water and the sugar dissolves. This tendency to dissolve may be regarded as a result of pressure exerted by the sugar molecules, and the solid is said to possess a *solution pressure*. Finally no more sugar will dissolve and the solution is saturated. There must then be some force which balances the solution pressure of the solid, and this force is the *osmotic pressure* which the dissolved substances exert in the solution. When the osmotic pressure is equal to the solution pressure, no more sugar will dissolve or, better stated, just as many molecules are precipitated as will dissolve during a given time. The process of dissolving sugar involves no electrical effect.

Like the sugar, though usually to a far less degree, a metal has a tendency to send out its atoms into a liquid which is in contact with it. This tendency is called its *electrolytic solution pressure*, because the metal forms positively charged cations and the metal becomes negatively charged with respect to the solution. In order that the metal may dissolve, its electrolytic solution pressure has to overcome the osmotic pressure of any cations of the same metal that may be present and, in addition, the electromotive force that results from the oxidation of the metal and formation of the positively charged cation. The potential difference between a metal and a solution is a quantity which can be measured easily; it is called the *oxidation potential* of the metal. The electrolytic solution pressure, on the other hand, cannot be measured directly; but if the oxidation potentials of various metals are measured against solutions of equivalent concentrations of the corresponding ions, in which it can be assumed that the osmotic pressures will be equal, these potentials will bear the same relation to one another as the electrolytic solution pressures. Just as in determining the height of an object it is necessary to choose some zero level from which to measure height, in the same way it has been found advisable to choose arbitrarily a zero level from which to measure the oxidation potential; the usual standard of comparison is the hydrogen electrode. The zero potential, according to this standard, is the potential of an electrode consisting of a strip of platinum, upon which some platinum black has been deposited electrolytically, half in pure hydrogen gas and half in normal sulfuric acid solution, which is assumed to furnish a molal solution of hydrogen ions. In accordance with this scale the oxidation potentials of some of the more common metals against molal solutions of their ions are:

ORIGINAL STATE	ELECTRODE REACTION	REDUCTION POTENTIAL, E, IN VOLTS
Lithium	$Li = \rightarrow Li^+ + e$	−3.02
Potassium	$K = \rightarrow K^+ + e$	−2.92
Sodium	$Na = \rightarrow Na^+ + e$	−2.71
Barium	$Ba = \rightarrow Ba^{++} + 2e$	−2.8
Strontium	$Sr = \rightarrow Sr^{++} + 2e$	−2.7
Calcium	$Ca = \rightarrow Ca^{++} + 2e$	−2.6
Magnesium	$Mg = \rightarrow Mg^{++} + 2e$	−1.55
Aluminum	$Al = \rightarrow Al^{+++} + 3e$	−1.34
Manganese	$Mn = \rightarrow Mn^{++} + 2e$	−1.08
Zinc	$Zn = \rightarrow Zn^{++} + 2e$	−0.76
Iron	$Fe = \rightarrow Fe^{++} + 2e$	−0.44
Cadmium	$Cd = \rightarrow Cd^{++} + 2e$	−0.40
Cobalt	$Co = \rightarrow Co^{++} + 2e$	−0.26
Nickel	$Ni = \rightarrow Ni^{++} + 2e$	−0.25
Lead	$Pb = \rightarrow Pb^{++} + 2e$	−0.14
Tin	$Sn = \rightarrow Sn^{++} + 2e$	−0.13
Hydrogen	$H = \rightarrow H^+ + e$	±0.00
Copper	$Cu = \rightarrow Cu^{++} + 2e$	+0.34
Silver	$Ag = \rightarrow Ag^+ + e$	+0.82
Gold	$Au = \rightarrow Au^+ + e$	+1.5

In the table, the positive sign is given when the metal is positive to the solution. This is the general practice among physicists, for if a cell is made up, as the Daniell cell, of copper dipping into molal copper sulfate at one electrode and zinc into molal zinc sulfate at the other electrode, a current will flow *in the wire* connecting the two strips of metal and the positive-to-negative direction will be from copper to zinc. The chemist, however, is used to considering solutions rather than the wire, and regards lithium and potassium as positive metals. He considers first the reaction in the solution and thinks of the positive-to-negative direction of the current as from the zinc to the copper *in the solution.* W. D. Bancroft has called attention to the confusion that is likely to arise if the usage is not uniform, and A. A. Noyes has used the positive signs against the voltages at the top of the table and called it a table of *Reduction Potentials.* This is perfectly logical.

Nernst, who first suggested the above explanation of the origin of the electromotive force and its relation to osmotic pressure, worked out an equation showing how the potential of a metal against a solution varies with the concentration of the ions of that metal in a solution which is in contact with the metal.

The derivation of the Nernst equation is omitted here because it can be found in most textbooks on *physical chemistry.* It states that the potential E between a metal and a solution of its ions can be expressed by the equation:

$$E = \frac{RT}{nF} \log_e \frac{c}{K}$$

where R is the gas constant in watt-seconds or joules, T is the absolute temperature, c is the ionic concentration, and K is a constant characteristic of the metal. Introducing for R its value 8.163 watt-seconds or joules and for F its value 96,500 coulombs, assuming a temperature of 30° (=303 absolute), and changing from natural logarithms to common logarithms by multiplying by 2.303, the equation becomes

$$E_{30} = \frac{0.060}{n} \log \frac{c}{K}$$

$$= \frac{-0.060 \log K}{n} + \frac{0.060 \log c}{n}$$

In a solution which is molar in its ions, the last term will disappear because the logarithm of 1 is zero. If, then, we measure the potential between a metal and a molar solution of its ions, we shall get the value

$$E_0 = \frac{-0.060 \log K}{n} = \text{the } \textit{normal oxidation potential}$$

which is a constant for any particular metal. The potential of the hydrogen electrode against a molar solution of its ions is arbitrarily given the value 0. It would have been better perhaps to call E_0 the *molar* electrode potential, for the word *normal* applied to electrode potentials does not refer to a *normal* solution of the ions.

The tables on pp. 95, 223, and 229 give the normal potentials or E_0 values. To find the oxidation potential at any other concentration we have from the Nernst equation

$$E_{30^\circ} = E_0 + \frac{0.060}{n} \log c$$

This expression can be used for computing the concentration of a solution when the electromotive force is known or for computing the electromotive force when the concentration is known. As the concentration is decreased from molal to tenth-molal the potential of the metal against the solution of its ions is lowered 0.060 volt if the ions are univalent, 0.030 volt if the ions are bivalent, and 0.020 volt if the ions are trivalent.

The theory of electrolytic solution pressure applies to electrolytic decomposition when the reverse action takes place. To effect a reduction of metal cations to metal, the oxidation potential or electrolytic solution pressure must be overcome. The actual decomposition potential required in electrolysis consists of the potential E_c required at the cathode and the potential E_a required at the anode for the liberation of oxygen or other oxidation that takes place. There is also the resistance of the electrolyte to be considered, which is usually negligible if the electrodes are near together and plenty of ions are present. The excess potential, E_s, required to overcome the resistance of the solution depends upon the current strength, for according to Ohm's law

$$I = \frac{E_s}{R} \quad \text{or} \quad E_s = IR$$

the potential E which the voltmeter shows when placed in circuit between the electrodes during electrolysis is

$$E = E_c + E_a + IR$$

and from this the current strength I can be computed

$$I = \frac{E}{R} - \frac{(E_c + E_a)}{R}$$

which is Ohm's law as it applies to electrolytes.

In the early days of electrolytic experiments, the chemist was usually content to know the difference in potential between the two electrodes, but recently more attention has been paid to the cathode potential. Since the total voltage required depends upon three independent factors, as shown in the equations just developed, it may happen that the cathode potential may change in a manner unfavorable for complete decomposition while at the same time the potential changes at the anode so that the total drop between the electrodes remains the same although the conditions become unfavorable at the cathode.

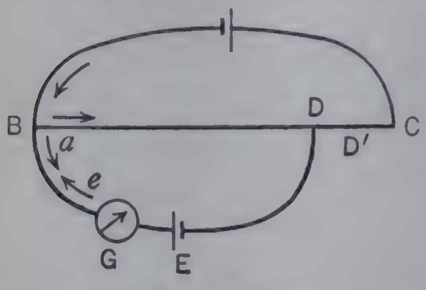

Fig. 32.

It may be well to explain the measurement of the single cathode potentials. This usually depends upon the measurement of a potential difference between two single potentials of which one is known. The ordinary method of measuring a potential difference is Poggendorff's *compensation method.* As source of current with a known and unchangeable electromotive force, a *standard cell* such as the *Weston cell* is used. One pole of this cell consists of mercury in contact with mercurous sulfate and the other of cadmium in contact with cadmium sulfate. The salts of these metals are not contained in solutions of varying concentrations, as in ordinary cells, but are present as solids in contact with saturated solutions. The solution always remains saturated with both salts so that the difference in potential between the two poles remains the same. The positive-to-negative direction of the current is from the mercury to the cadmium in the wire. The potential of the cell is 1.0183 at 20° when the solution is saturated with $CdSO_4$.

The measurement of the electromotive force is carried out as follows: A circuit is established consisting of a storage cell or accumulator *A*, Fig. 32, and a wire *BC* of uniform cross section and high resistance; there prevails in the wire between one end of it, *B*, and any other point *D*, *D′*, or *C* a certain drop in potential which can be measured with the aid of the standard cell. To do this, another electric circuit *BGED*, containing the standard cell *E* and a sensitive galvanometer *G*, is connected in such a way that the current in this second circuit flows in the opposite direction *e* to that of the other current which has the direction *a*. Then, by moving the sliding contact *D* along the wire *AC*, a point will be found for which the galvanometer *G* shows the passage of no current. The drop in potential between *B* and *D* is equal to the electromotive force of the standard cell, namely 1.0183 volts at 20°.

If, now, in place of the standard cell *E*, an unknown electromotive force E_x is introduced and the sliding contact is moved to a point *D′* to make the galvanometer reading zero, then the unknown electromotive force E_x bears the same relation to that of the standard cell as the length of wire *BD* is to the length *BD′*, that is

$$E_x = 1.0183\,\frac{BD'}{BD}$$

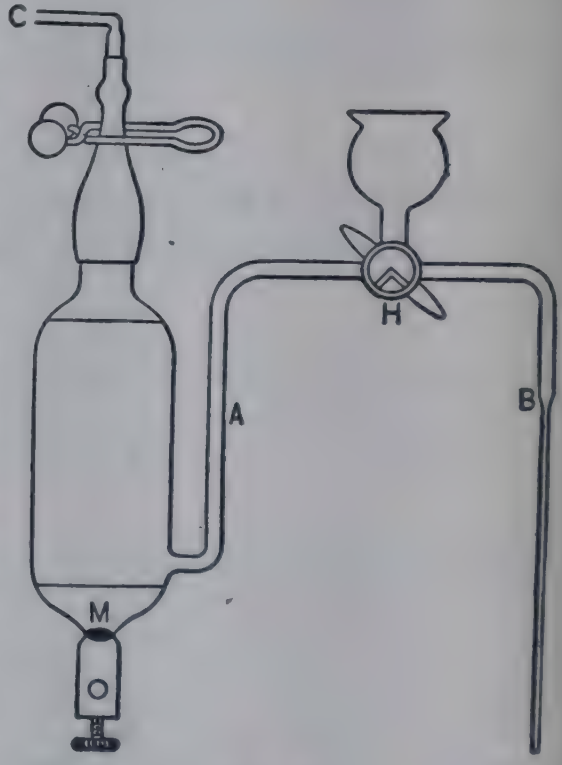

Fig. 33.

To measure the single potential between a metal and a solution, it is necessary to use the metal in the solution as one electrode and to combine it with another electrode of known potential, such as the normal calomel electrode, one form of which is shown in Fig. 33. The bottom of the vessel is covered with a layer of pure mercury, about 0.5 cm deep; on top of this is a little calomel (Hg_2Cl_2) which has been moistened with normal potassium chloride and triturated with a little mercury to form a paste, and then the vessel is filled with normal potassium chloride solution[1] which has been saturated with calomel by prolonged shaking. In the layer of mercury at the bottom, electrical connections made by means of platinum wire fused in the glass.[2] The potential of the unknown electrode is measured with the calomel electrode as outlined above, and from the result the known potential of the calomel electrode is deducted. It is assumed that the resistance of the solution can be neglected as well as that of the lead wires.

The reaction between a metal and a solution is a reversible one, taking place in one direction when the metal dissolves and in the opposite direction when the metal is deposited electrolytically. It follows the mass-action law, as the Nernst equation shows. Just as the table of solubility products shows how the ions can be separated by precipitation, so the table of electrode potentials gives information concerning the behavior in electrolysis. In the potential series table, the potential of cadmium in a molal solution of Cd^{++} is given as -0.40 volt, of hydrogen against molal H^+ it is 0.00, and of copper against molal Cu^{++}, $+0.34$. This means that, with respect to these three ions in electrolysis, copper is deposited most easily and cadmium least easily; the formation of hydrogen gas from hydrogen ions is easier than the deposition of cadmium but harder than the deposition of copper. Is it possible to deposit copper completely without getting any hydrogen gas liberated?

The Nernst formula tells us that the discharge potential increases as the solution of copper ions becomes more dilute: $E_{30°} = +0.31 + (0.060 \div 2) \log c$, in which equation c is the molal concentration of copper ions and $+0.31$ is the decomposition potential from a molal solution of copper ions. When less than 0.1 mg of copper is in solution, we may say that the deposition is complete. A concentration of 0.06 mg of copper in, say, 100 ml of electrolyte corresponds to $c = 0.00001$, and $(0.058 \div 2) \log c = -0.15$ volt. Adding -0.15 volt to $+0.31$ volt gives $+0.16$ volt, which shows that copper can be completely deposited,

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[1] The concentration of the potassium chloride solution is important because the potential of the calomel electrode varies with the concentration of the mercuric chloride owing to its effect upon the solubility and ionization of calomel and of the conductivity. Three concentrations of potassium chloride have been used: a saturated solution, a normal solution, and a tenth-normal solution. The potentials vary as follows:

	20°	25°	30°
0.1 Normal	+0.3379	+0.3376	+0.3372
Normal	+0.2860	+0.2848	+0.2836
Saturated	+0.2496	+0.2458	+0.2427

[2] Sometimes a narrow tube is used dipping in the mercury with a platinum wire at the bottom where the tube is sealed.

by controlling the cathode potential carefully, without any liberation of hydrogen gas from a molal solution of hydrogen ions. Experiment shows that this is true, although in an ordinary electrolytic experiment the solution becomes impoverished in copper ions in the vicinity of the cathode and the voltage used is sufficient to liberate hydrogen so that, unless the solution is very well stirred, some hydrogen gas is evolved before the last trace of copper is deposited; but by continuing the electrolysis a little longer, to give the copper ions time to reach the electrode, even this last portion is reduced. In general we may say that it is possible to effect a quantitative separation electrolytically, if the cathode potential is carefully watched with the aid of a calomel electrode, when there is 0.2-volt difference in decomposition potential of the cations present. In an acid solution, no cadmium will be deposited because the decomposition potential of cadmium from a molal solution is +0.44 and it is easier to discharge hydrogen ion.

From an alkaline solution containing potassium cyanide, on the other hand, cadmium can be deposited in the presence of copper. In this case the cadmium is present as $Cd(CN)_4^{--}$ and the copper as $Cu_2(CN)_6^{----}$. In normal potassium cyanide solution, the concentration of Cd in a molal solution has been estimated to be 10^{-17}, and that of Cu to be 10^{-26}. Although the oxidation potential of copper in a molal solution of cuprous ions is +0.51 volt, it is $0.5 - (26 \times 0.06) = -1.05$ volts in the normal potassium cyanide solution whereas the potential of the cadmium electrode is $-0.44 - (17 \times 0.03) = -0.95$ volt. By making the solution stronger in potassium cyanide, a quantitative deposition of cadmium can be accomplished in the presence of copper.

So far the discussion has been concerned almost entirely with cathodic deposition, but the same principles hold with respect to anodic oxidations. Some of the reactions that can be accomplished at the anode are:

$$2H_2O \rightarrow 4H^+ + O_2 \uparrow + 4e$$
$$Pb^{++} + 2H_2O \rightarrow \mathbf{PbO_2} + 4H^+ + 2e$$
$$2Cl^- \rightarrow Cl_2 \uparrow + 2e$$
$$Cu \rightarrow Cu^{++} + 2e$$
$$\mathbf{Mn} + 8CO_3^{--} + 4H_2O \rightarrow MnO_4^- + 8HCO_3^- + 7e$$

The mass-action law and the Nernst equation come into consideration here as in the cathodic reductions. The decomposition voltages and the concentration relations and the nature of the electrode determine the reaction that will take place under given conditions.

The voltage series and the Nernst equation, moreover, apply to every reaction of oxidation and reduction. Just as a cell can be made consisting of metallic zinc in zinc sulfate as one electrode and copper in copper sulfate as the other, so a cell can be made up, for example, with a platinum electrode dipping in a dilute acid potassium dichromate solution and platinum dipping in hydrogen sulfide water. The oxidation of the sulfide and reduction of the dichromate will take place in separate beakers if the electrodes are connected by external wires and electrical contact is maintained between the two solutions by means of a tube containing a neutral salt (salt bridge). Then again, to show the application of the Nernst formula, a cell can be constructed with silver dipping in tenth-molar silver salt as one electrode and silver dipping in hundredth-molar silver nitrate as the other electrode. In the dilute solution, silver will dissolve; in the concentrated solution, silver will be deposited; and the positive-to-negative direction of the current in the wire will be from the concentrated solution to the dilute one.

The following table shows some potentials of oxidation reactions other than those of dissolving metals:

Original State	Electrode Reaction	E, in Volts
S^{--}	$S^{--} \rightarrow S + 2e$	−0.51
Cu^{+}	$Cu^{+} \rightarrow Cu^{++} + e$	+0.17
I_2 (solid)	$I_2 + 12OH^{-} \rightarrow 2IO_3^{-} + 6H_2O + 10e$	+0.21
Hg_2Cl_2(solid)	**Hg_2Cl_2** $+ 2Cl^{-} \rightarrow 2HgCl_2 + 2e$	+0.24
OH^{-}	$4OH^{-} \rightarrow O_2 + 2H_2O + 4e$	+0.41
Br_2 (liquid)	$\frac{1}{2}Br_2 + 6OH^{-} \rightarrow BrO_3^{-} + 3H_2O + 5e$	+0.51
MnO_2 (solid)	**MnO_2** $+ 4OH^{-} \rightarrow MnO_4^{-} + 2H_2O + 3e$	+0.52
Br^{-}	$Br^{-} + 6OH^{-} \rightarrow BrO_3^{-} + 3H_2O + 6e$	+0.60
Fe^{++}	$Fe^{++} \rightarrow Fe^{+++} + e$	+0.75
H_2O_2	$H_2O_2 \rightarrow O_2 + 2H^{+} + 2e$	+0.80
Cl_2 (gas)	$Cl_2 + 2OH^{-} = 2HClO + 2e$	+0.85
NO (gas)	$NO + 2H_2O \rightarrow NO_3^{-} + 4H^{+} + 3e$	+0.95
Br^{-}	$2Br^{-} \rightarrow Br_2 + 2e$	+1.08
Cl^{-}	$Cl^{-} + OH^{-} \rightarrow HClO + 2e$	+1.10
I_2 (solid)	$I_2 + 6H_2O \rightarrow 2IO_3^{-} + 12H^{+} + 10e$	+1.19
Cr^{+++}	$Cr^{+++} + 4H_2O \rightarrow HCrO_4^{-} + 7H^{+} + 3e$	+1.3
Cl^{-}	$2Cl^{-} = Cl_2$ (gas) $+ 2e$	+1.35
Pb^{++}	$Pb^{++} + 2H_2O \rightarrow$ **PbO_2** $+ 4H^{+} + 2e$	+1.44
Cl^{-}	$Cl^{-} + H_2O \rightarrow HClO + H^{+} + 2e$	+1.51
Mn^{++}	$Mn^{++} + 4H_2O \rightarrow MnO_4^{-} + 8H^{+} + 5e$	+1.52
MnO_2 (solid)	**MnO_2** $+ 2H_2O \rightarrow MnO_4^{-} + 4H^{+} + 3e$	+1.63
Co^{++}	$Co^{++} \rightarrow Co^{+++} + e$	+1.8
Cl_2 (gas)	$Cl_2 + 2H_2O \rightarrow 2ClO^{-} + 4H^{+} + 2e$	+1.8
O_2 (gas)	$O_2 + H_2O \rightarrow O_3 + 2H^{+} + 2e$	+1.9
F^{-}	$2F^{-} = F_2 + 2e$	+1.96

In using this and the preceding table of oxidation potentials, it is necessary to remember that, when a cell is made up from any two of the elements in the tables, the positive-to-negative direction in the wire connecting the terminals will always be from the lower to the higher member. Often an element can undergo several stages of oxidation. Thus iron can be oxidized to ferrous salt ($E = -0.43$), and the ferrous salt can be oxidized to ferric salt ($E = +0.75$). This shows that it is harder to oxidize the ferrous salt than the original iron; and, in fact, even hydrogen ions will accomplish the first oxidation. What will be the reduction potential of iron against a molal solution of *ferric* ions? To make this computation it is only necessary to remember that the work done is the same whether the oxidation takes place in one stage or in two stages, and work is measured by multiplying the quantity of electricity, in coulombs, by the voltage. In the first stage of the iron oxidation, 2 faradays are involved for each gram-atom of iron, and in the second stage only 1 faraday. We can say, therefore, when x is the unknown potential:

$$2e \times (-0.43) + e \times 0.75 = 3e \times x$$
$$3\,x = -0.11 \qquad x = -0.037$$

Current Density. If too much current is used during an electrolysis, the deposit is likely to come down spongy and non-adherent. This is usually due to the fact that gas is being evolved at the cathode while the metal is being deposited because the solution becomes temporarily deficient in the ions of the metal which it is desired to determine. The amperage used per 100 sq cm of electrode surface is called the *current density* and is usually designated by the symbol ND_{100}. To prevent the formation of spongy deposits it was formerly customary to use a small current and electrolyze for a long period. To avoid the expenditure of so much time, it is necessary to use more current. The harmful effects of too high current density can be overcome by using more concentrated solutions, stirring the electrolyte, and by using gauze electrodes with which considerable surface is exposed and the electrolyte flows through the meshes of the electrode. Stirring is usually accomplished by rotating one of the electrodes.

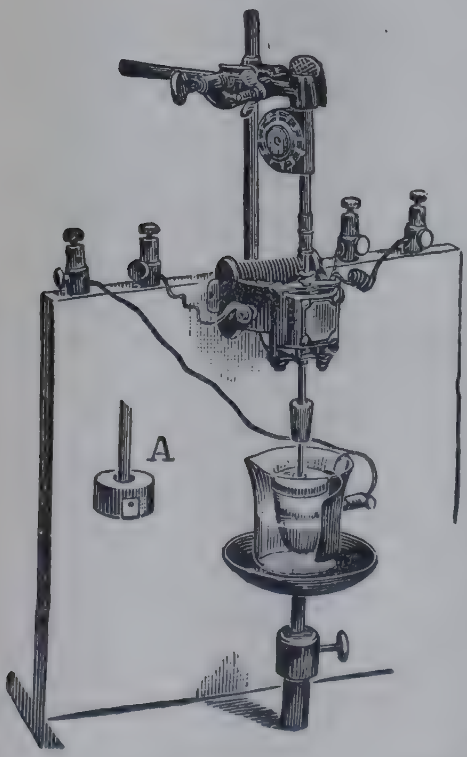

FIG. 34.

Electrodes. Various types of platinum electrodes have been recommended. F. A. Gooch used with excellent success the outfit shown in Fig. 34; the cathode is a 20-ml platinum crucible which can make 800 revolutions per minute, and the anode is a platinum plate. A narrow strip of platinum foil is soldered to the shaft and bent upward along the sides of the rubber stopper which holds the crucible, thus making electrical connection between the shaft and crucible. Very often a 125-ml platinum dish is used with electrical connection so that it serves as one of the electrodes as well as to contain the electrolyte.

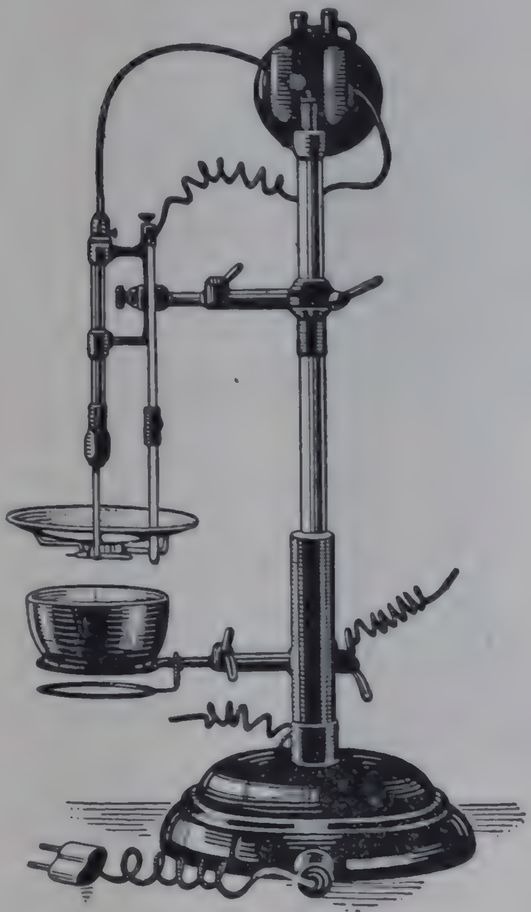

FIG. 35.

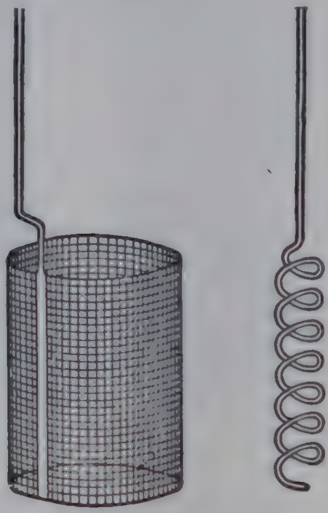

FIG. 36.

The outfit shown in Fig. 35 has been much used in Germany. Cl. Winkler recommended a cylindrical gauze electrode as cathode and a stout platinum wire wound into a spiral as anode (Fig. 36), and these forms have become popular. Gauze anodes of similar size are also used. At the Massachusetts Institute of Technology the Braun electrolytic apparatus (Fig. 37 on p. 232) is used with gauze cathodes and gauze anodes.

Determination of Copper, Lead, and Zinc in Brass

The best brass alloys contain very little tin, lead, iron, or nickel. In commercial laboratories, often the copper and lead contents are determined electrolytically and the zinc is determined *by difference*, that is, by subtracting the percentages of copper and lead from 100 per cent.

The following method of analysis, however, provides for the determination of copper, lead, tin, iron, and zinc and is capable of giving accurate results.

Weigh 0.9–1.0 g of the alloy into a slender beaker of about 150-ml capacity. Add 12 to 15 ml of 6 N nitric acid, cover the beaker, and heat

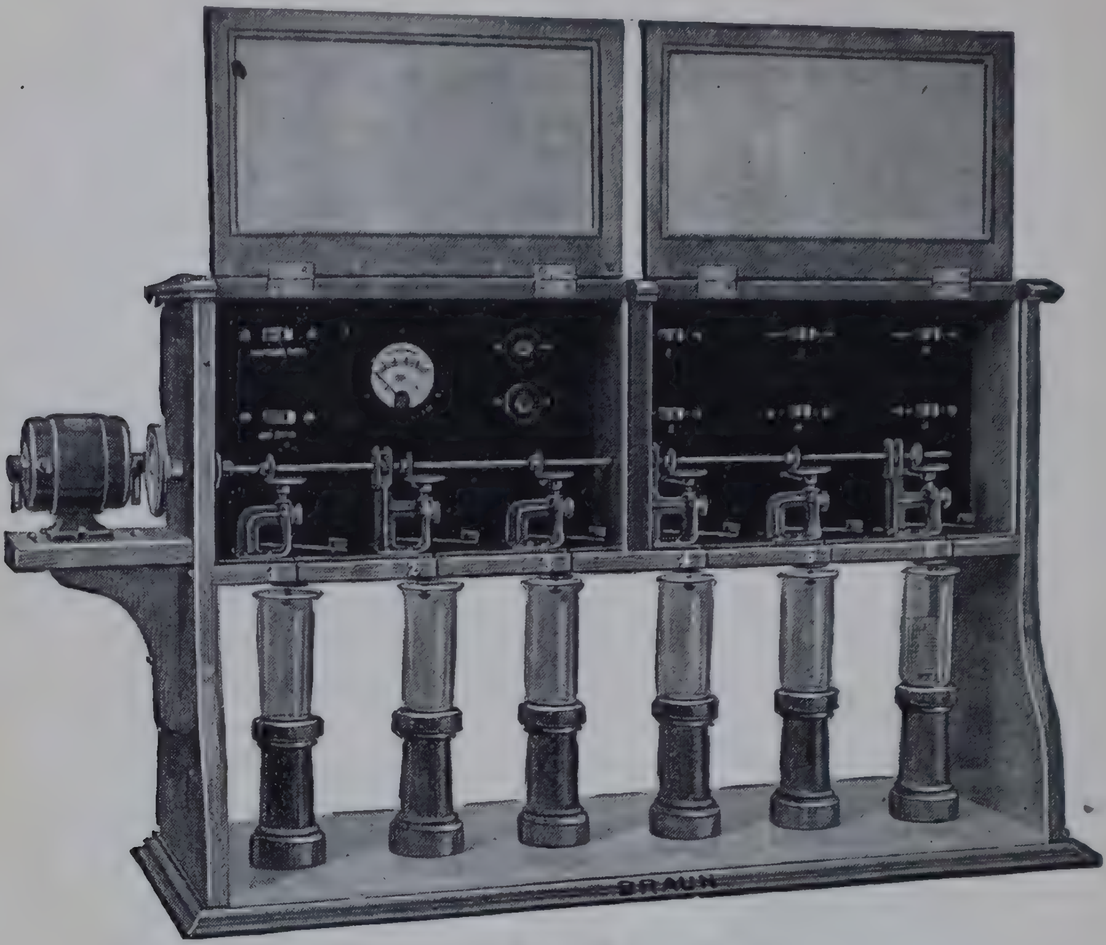

FIG. 37.

gently till all the brass is dissolved. If a clear solution is obtained, no tin is present, and the solution after dilution is ready for electrolysis.

If a white precipitate of metastannic acid forms, evaporate the solution just to dryness but do not bake the residue. Add 2 ml of 6 *N* nitric acid, dilute with 25 ml of water, and boil gently to dissolve the nitrates of copper and zinc. Filter off the metastannic acid, wash it with hot water, ignite in a porcelain crucible, and weigh as SnO_2.

Dilute the clear solution of the nitrates to 100 ml and boil gently for 1 minute to remove any nitrous oxides. Wash down the sides of the beaker and the cover glass, allow to cool a little, and then cautiously add small portions of solid urea until there is no more evolution of gas:

$$2HNO_2 + CO(NH_2)_2 = 3H_2O + CO_2 + N_2$$

Attach the weighed gauze electrodes to the binding posts of the electrolytic apparatus, put the beaker in place. Make sure that the cathode reaches to the bottom of the beaker and that the anode can rotate freely inside the cathode. Turn on the stirrer and turn the switch with the rheostat adjusted to give a current of 1.8–2.0 amperes. After the solution has become colorless, continue the electrolysis 10 minutes longer. The electrolysis ought not to require more than 45 minutes at the most.

Wash the electrodes while lowering the beaker and while the current is still flowing. Dip them in alcohol and dry a very short time in the hot closet at 105°. The deposit on the cathode is pure copper, and that on the anode is lead dioxide, PbO_2.

To make sure that all the copper has been deposited, add a slight excess of ammonia to the entire solution. If a blue color is noticeable,[1] make acid with dilute sulfuric acid and electrolyze with clean electrodes until all the copper is removed.

The electrolysis can take place without stirring. In this case use 0.15 ampere of current and electrolyze over night.

Test for Iron and Aluminum

To the electrolyzed solution add a little bromine water, to make sure that any iron is in the ferric condition, and enough ammonia to dissolve the zinc hydroxide precipitate that may form at the neutral point. If any precipitate of ferric or aluminum hydroxide forms, filter it off. To make sure that no zinc hydroxide is in the precipitate, redissolve the precipitate in a little hot 2 N hydrochloric acid, dilute to 50 ml, and precipitate again by adding ammonia. Ignite and weigh the precipitate as Fe_2O_3. If there is any likelihood of aluminum being present, examine the ignited oxides as described on p. 209.

Determination of Zinc

Procedure. To the *cold* acid solution of the zinc salt add ammonium hydroxide until the solution is barely acid to methyl orange. Care is necessary at this point, as zinc ammonium phosphate is soluble both in acids and ammonia. Sometimes nitrous acid which is present decomposes the indicator and makes it difficult to tell the methyl orange color change. Make sure that the neutralized solution has no appreciable odor of ammonia, after blowing away the fumes. Dilute with water, if necessary, to a volume of 150 ml, and heat on the water bath. To the hot solution add 3 g of $(NH_4)_2HPO_4$ dissolved in a little water. The precipitate that first forms is amorphous and does not settle out, but it soon changes to finely crystalline $ZnNH_4PO_4$ which settles well and leaves a clear supernatant liquid. The transformation takes place more rapidly in proportion to the quantity of ammonium salt present. After the heating has continued for about 15 minutes, remove the dish from the water bath, and when the precipitate has settled for a short time filter off the precipitate into a weighed filtering crucible, wash 6 times with hot 1 per cent ammonium phosphate solution, then twice with cold water, and finally with 50 per cent alcohol. Dry at 100–135° for an hour and weigh as $ZnNH_4PO_4$, which contains 36.64 per cent Zn. The precipitate can be washed and dried with alcohol and ether if desired (cf. p. 192).

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[1] A pale blue color may indicate the presence of nickel but usually is caused in brass analysis by a little copper which has escaped deposition.

The precipitate can also be weighed as the pyrophosphate, $Zn_2P_2O_7$, in which case it is desirable to heat the dried zinc ammonium phosphate very slowly in an electric oven to 900–1000°. If such an oven is not at hand place the filtering crucible in a larger crucible and heat over the gas flame. Gradually raise the temperature until finally the full heat of the Teclu or Méker burner is reached. Heat to constant weight after cooling in a desiccator. Before using the filtering crucible, it must be heated, cooled, and weighed in the same way. $Zn_2P_2O_7$ contains 42.90 per cent Zn.

Test the filtrate from the $ZnNH_4PO_4$ precipitate with ammonia and ammonium sulfide. If a small precipitate of white zinc sulfide is formed, filter it off, using an ashless paper filter, ignite in a porcelain crucible, and weigh as ZnO. No sulfide precipitate will be formed if the above conditions have been followed carefully.

Titrimetric Determination of Lead in Brass

Dissolve 5 g of brass in 50 ml of 6 *N* HNO_3. (If an appreciable quantity of metastannic acid separates and gives a turbid solution, remove it as directed on p. 232.) To the solution add 15 ml of 18 *N* H_2SO_4 and evaporate on the hot plate, without boiling, until fumes of H_2SO_4 are evolved. Allow to cool, carefully wash down the sides of the beaker, and again evaporate to fumes. Do not cover the beaker tightly during the evaporation because, if water condenses on the bottom of the watch glass and later drops into the hot acid, there will be spattering. After all nitric acid has been expelled by this double evaporation, cool, add 100 ml of water, mix well, add 30 ml of alcohol, and allow to stand at least 1 hour. Filter through a paper filter and wash the precipitate of $PbSO_4$ with 0.7 per cent ammonium sulfate solution or with 1.8 *N* H_2SO_4.

With the aid of the wash bottle, transfer as much of the precipitate as possible to a 300-ml beaker, replace the funnel, and, with the 300-ml beaker under it, dissolve the $PbSO_4$ on the filter in not more than 25 ml of hot 3 *N* ammonium acetate solution as follows: Pour about 5 ml of hot acetate solution upon the upper part of the filter and wash with about 10 ml of hot water from the wash bottle. Repeat this treatment three times. Then treat with another portion of ammonium acetate solution and test the filtrate that now runs through the filter with a few drops of K_2CrO_4 solution. If a precipitate forms, save it and continue the treatment with ammonium acetate solution and hot water until a negative test is obtained.

Make the ammonium acetate solution acid with about 2 ml of 6 *N* acetic acid, heat to boiling, and add 5 ml of 5 per cent $K_2Cr_2O_7$ solution. Boil gently for 5 minutes, filter, and wash ten times with hot water. The last washings should show no yellow color. Place a clean beaker under the funnel and dissolve the $PbCrO_4$ in 12–15 ml of cold 6 *N* HCl added in small portions and with intermediate washing with water. The acid must be cold to avoid reducing some of the chromic acid to chromic salt. All yellow color must be removed from the filter, but it does no harm if some white $PbCl_2$ remains. Continue washing until about 100 ml of filtrate has been collected. Add to the solution 2 g of KI, and titrate the liberated iodine with standardized $Na_2S_2O_3$ solution. One milliliter of 0.1 *N* $Na_2S_2O_3$ = 0.006907 g Pb.

HOME PROBLEMS

116. A 100-watt, 110-volt incandescent lamp is connected in series with an electrolytic cell. What weight of cadmium could be deposited from solution by the current in 30 minutes, assuming the resistance of the lamp to be unchanged?

117. What weights of Cu, of Zn, and of PbO_2 will be deposited in separate electrolytic cells assuming 100 per cent current yield by a current of 0.08 ampere flowing for 30 hours?

118. What quantity of electricity is required for (*a*) the electrolytic deposition of 1.196 g of PbO_2; (*b*) the liberation of 0.800 g of oxygen gas; (*c*) the liberation of 30.0 ml of chlorine when measured under standard conditions?

119. On the basis of 30 per cent current yield, compute the cost of the power required to produce 1 lb of $NaMnO_4 \cdot 3H_2O$ from a manganese anode and 0.3 *N* Na_2CO_3 solution. Emf = 8 volts. Cost of current = 3 cents per kilowatt-hour.

120. Caustic potash is to be produced by the electrolysis of a solution of KCl, and a solution containing 100 g of KOH per liter is required. An average current of 900 amperes is used, and, at the end of 5 hours, 102 l of caustic potash solution has been produced, a small portion of which on analysis is found to be 1.52 *N* as an alkali. How much longer must the electrolysis be continued in order to produce the desired concentration, and what is the current efficiency at the cathode?

121. Pure crystals of $CuSO_4 \cdot 5H_2O$ are dissolved in water and the solution is electrolyzed with an average current of 0.60 ampere. The electrolysis is continued for 5 minutes after all the copper has been deposited, and it is found that a total volume of 62.5 ml of gas (H_2 and O_2), measured dry at 18° C and 745 mm pressure, has been evolved. What weight of crystals was taken for electrolysis? (Assume that all the copper is deposited before hydrogen is evolved.) How many milliliters of 0.1 *N* NaOH will the resulting solution neutralize?

122. What weights of Cu from $Cu_2(CN)_2$, Cu from $CuSO_4$, Zn from $Zn(NH_3)_4SO_4$, Ag from $KAg(CN)_2$, Fe from $FeCl_3$, and MnO_2 from $MnSO_4$ solutions can be deposited at 100 per cent current efficiency by 0.08 ampere during 30 hours?

123. The Cr in a sample of chromate weighing 1.12 g is determined with the aid of a mercury cathode. If the sample does not contain over 80 per cent of Na_2CrO_4, and if 70 per cent of the current used is lost by evolution of H_2, how long should the analysis be continued with a current of 0.11 ampere?

124. The passage of 1 ampere-hour through a $NiSO_4$ solution caused the deposition of 0.0342 electrochemical equivalent of Ni. If the rest of the current served to liberate H_2 at the cathode, compute its volume at 27° and 750 mm pressure.

125. After all the Cu was deposited from a solution of pure $CuSO_4 \cdot 5H_2O$ crystals in water, the electrolyte required 60.0 ml of 0.5 *N* NaOH for neutralization. If the electrolysis was prolonged so that the final current efficiency was only 40 per cent, compute (*a*) the actual time of electrolysis with a current of 0.12 ampere, (*b*) the weight of Cu deposited, (*c*) the weight of blue vitriol used, (*d*) the volume of H_2

evolved at 27° and 750 mm, and (*e*) the volume of O_2 evolved under the same conditions. Compute the percentage error if the gases were measured over water (disregarding the solubility of the gas in water).

126. A concern plates 10,000 spoons daily, depositing 5 g of Ag on each spoon and using an emf of 4 volts. With a current efficiency of 88 per cent and a cost of 1.5 cents per kilowatt-hour, compute the monthly bill (25 days) for electrical energy.

127. To check up the current efficiency of a process for depositing Cd, the cell was placed in series with a gas coulometer. During the time that 1.786 g of Cd was deposited, 720 ml of wet H_2 gas was evolved, measured at 17° and 770 mm pressure. Calculate the current efficiency.

128. If the oxidation potential of Fe°/Fe^{++} is -0.43 in molal solution and Fe°/Fe^{+++} is -0.04, compute the value of Fe^{++}/Fe^{+++}.

CHAPTER XIV

ANALYSIS OF SILICATES

Preparation of the Substance for Analysis

Break up large pieces of rock on a thick steel plate with a specially hardened surface and a similarly hardened pounder, such as street pavers use. Place the small fragments in a " diamond " mortar or in one like that shown in Fig. 38. It is made of chilled and case-hardened tool steel. The dimensions of the block *A* are 12.5 by 12.5 by 6 cm, and there is a depression in the center 0.6 cm deep. The pestle *B* is 20 cm high, and the diameter at the base is 3.5 cm. The cylinder *C* is 12.5 cm tall and of 5-cm outside diameter accurately fitting the depression in the block. Unlike the ordinary " diamond " mortar, the pestle has a smaller diameter than the inside diameter of the cylinder, which is 4.4 cm. The crushing is done with the pestle, without the aid of a hammer. With this mortar most of the sample can be reduced fine enough to pass through silk bolting cloth.

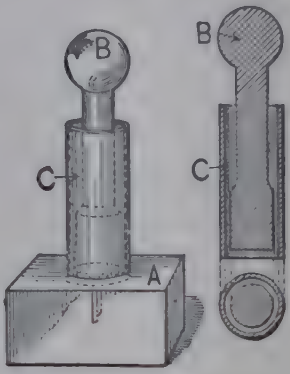

FIG. 38.

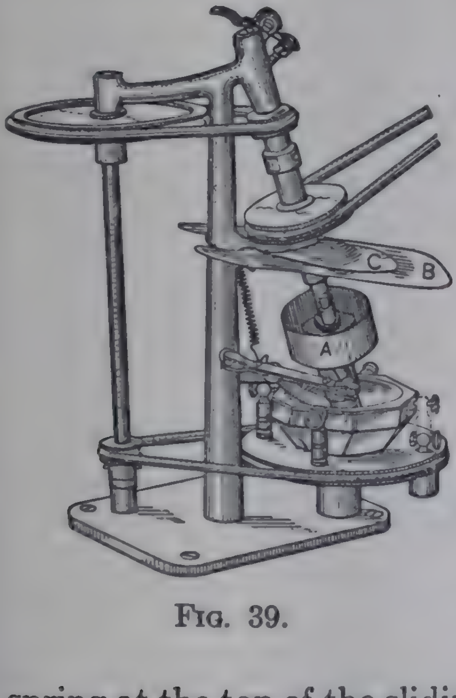

FIG. 39.

A finer powder can be obtained by hand grinding in an agate mortar, but the McKenna ore grinder shown in Fig. 39 is more economical in the long run. *A* is a copper cup soldered to the head of the pestle holder and assumes, without friction, the motion of the latter. *B* is a tin plate with deep sinus and is covered by the rubber cloth *C* which fits closely about the metal shaft. These attachments *A*, *B* and *C* prevent oil and dust from the belts and bearings from entering the mortar. The spring at the top of the sliding rod, to which the agate mortar is attached at the bottom, can be adjusted to give any desired pressure or can be thrown back to allow the pestle to be raised in removing the agate mortar. The pestle makes about 200 revolutions per minute, and the mortar moves slowly in the same direction. The scraper keeps the material in the center, and the combined rolling and sliding motion reduces the hardest ore very quickly.

Do not attempt to grind too much at one time, and frequently sift through silk bolting cloth to prevent as much as possible contaminating the sample by abrasion and loss of moisture by the heat of grinding. Prepare at least 5 times as much sample as is needed, and make sure that all the powder is included; it is never admissible to take only the powder that passes through the sieve the first time. Mix well by rolling on a sheet of glazed paper, rubber, or oilcloth. A corner of the sheet is lifted and drawn across, low down, in such a way that the material is made to roll over and over and does not merely slide along. The sample should be rolled back and forth along each diagonal for 100 times or more. Then the sample may be spread out into squares and a little taken from each square. Finally mix the sample chosen.

Weighing the Substance. It has been customary to dry the powder before weighing at 100–110° until a constant weight is obtained. If there is danger of losing combined water by this procedure, it has been recommended that the powder be dried in a vacuum over concentrated sulfuric acid. The practice of drying the substance in either of the above ways, however, is to be discountenanced. It is far better to use the air-dried substance for the analysis, and to determine the moisture in a separate sample. This is more accurate, because the dry silicate powder is hygroscopic, so that a portion weighed out today is likely to contain a different amount of moisture from one taken tomorrow, and this discrepancy is avoided when the air-dried powder is taken for the analysis. Further, as Hillebrand had conclusively shown, chemically combined water is likely to be expelled not only by heating at 100° but also by drying in a vacuum over sulfuric acid. This is particularly true of the zeolites. In orthoclase, however, only about 0.1 per cent of moisture is present, so that with this particular substance accurate results will be obtained by either method.

For the analysis weigh out to the nearest 0.1 mg two portions of about 0.5 g each. The first serves for the determination of SiO_2, $Al_2O_3 + Fe_2O_3$, CaO, and MgO; the second, for that of the alkalies.

Fusion with Sodium Carbonate

Fuse 0.5 g of the very finely powdered substance in a platinum crucible with 3 g of sodium carbonate. The powdered silicate should be intimately mixed with the flux and a little sodium carbonate sprinkled on top. Heat the covered crucible at first over a small flame to drive out any moisture present. Gradually raise the temperature until finally the highest heat of a good Tirrell or Méker burner is obtained. As soon as the mass melts quietly and there is no further evolution of carbon dioxide, the decomposition is complete. Wind a piece of platinum wire into a spiral and insert it into the fused mass. Remove the flame, allow the crucible to cool in the air somewhat and then play a stream of water upon the outside of the crucible. As soon as the crucible does not hiss when the water strikes it, quickly introduce enough water into the crucible to cover the melt. After about a minute carefully pull on the wire; usually the melt can be withdrawn from the crucible. If it does not come out easily, it can often be loosened by carefully heating the crucible.[1] Place the melt in a 300-ml casserole, add 25 ml of water, cover the casserole, and carefully add 25 ml of 6 *N* hydrochloric acid. A lively evolution of carbon dioxide at once takes place, but as the silicic acid separates, the inner part of the cake gradually becomes coated with a film of silicic acid which protects it from the further action of the acid. Consequently it is necessary to break up the cake from time to time, by means of a glass rod, until finally there is no further evolution of a gas and no more hard lumps remain. When manganese is present the melt is colored green with manganate and the solution may be pink at first with permanganate but the permanganate gradually decomposes during the subsequent heating. After the evolution of carbon dioxide has nearly ceased, wash off the under side of the watch glass, raise it by placing a glass triangle under it, and evaporate to dryness. Heat the residue for at least an hour in the hot closet at 120–130°, to dehydrate the silica.

Moisten the dry powder with concentrated hydrochloric acid, and allow the covered dish to stand for 10 minutes at the ordinary temperature in order that basic salts and oxides formed during the evaporation and drying may once more be changed to chlorides. Then warm gently, dilute with 100 ml of water, heat to boiling, and, after the silicic acid has settled, filter through a well-fitting ashless paper filter. Wash the residue three or four times by decantation, with hot 2 *N* hydrochloric acid, then transfer to the filter and wash with hot water until free from chloride. Place the precipitate in a platinum crucible and set aside for the time being. The separation of the silicic acid is not quite complete; as much as 2 mg may remain in the filtrate. To remove this, once more evaporate the solution to dryness on the water bath, and again heat at 120–130°, for an hour, moisten the residue with 5 ml of concentrated hydrochloric acid, and allow to stand not more than 15 minutes.[1] Warm, dilute to 100 ml, heat to gentle boiling, and filter through a new and correspondingly small, ashless filter, washing with hot 2 *N* acid and with water as before. Combine this filtrate with that previously obtained and analyze it for Fe_2O_3, Al_2O_3, CaO, and MgO as described on p. 208. Ignite the wet filters containing the silica in a platinum crucible. Keep the temperature low till all the carbon is consumed, and do not allow the filter to catch fire. Finally cover the crucible, and ignite over the blast lamp or over a Méker burner.

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[1] If the fusion cannot be removed from the crucible, place it, together with its cover, in the beaker, and treat with dilute acid as described.

Remark. It is not advisable to use suction in filtering silicic acid. If the precipitate is allowed to dry before being placed with the filter in the crucible there is danger of losing some of the fine powder. The heating at 120° decreases the solubility of the silica in acid, but this temperature should not be exceeded. Magnesia at a higher temperature recombines with silica, and iron and aluminum oxides are formed in a condition hard to dissolve.

Testing the Purity of the Silica

The silica thus obtained is never absolutely pure, except in the analysis of a water-glass. Its purity must always be tested. For this purpose moisten it with water;[2] then add a drop of concentrated sulfuric acid and about 5–10 ml of pure hydrofluoric acid. Do not measure the acid in a glass graduate; do not inhale the fumes any more than is necessary; and if any hydrofluoric acid is spilled on the hands wash them immediately under the water tap. Place the crucible in an air bath and evaporate under a good hood until no more vapors are expelled. Then remove the excess of sulfuric acid by heating over a free flame. Raise the temperature gradually, and finally heat the crucible over a blast lamp or Méker burner, and again weigh. Repeat the treatment with sulfuric and hydrofluoric acids, without adding any more water, until the contents of the crucible (usually Al_2O_3, Fe_2O_3, TiO_2, ZrO_2, V_2O_5, P_2O_5, etc.) are at a constant weight. Deduct this amount from the weight of impure silica and add it to the precipitate obtained with ammonia in the subsequent analysis. The precipitate of Fe_2O_3, Al_2O_3, etc., should then be tested for SiO_2 by fusing the weighed precipitate with $KHSO_4$, treating the melt with dilute sulfuric acid, filtering, and testing the residue with hydrofluoric acid.

A great many silicates are incompletely decomposed, if at all, by direct treatment with hydrochloric acid in an open vessel. Inasmuch as it is necessary to test the purity of the silica by treatment with sulfuric and hydrofluoric acids, it might seem unnecessary to try to get a pure silicic acid residue before applying this treatment. Undecomposable silicates are likely to contain some alkali and alkaline-earth metal as well as iron and manganese in combination with silica. When such a silicate is treated with sulfuric and hydrofluoric acids, the alkali and alkaline earths are left as sulfates, the iron is left as Fe_2O_3, and the manganese as Mn_3O_4. Moreover, boron is volatilized as BF_3. Only when the silica is nearly pure and when the impurities are left as oxides in the same state of oxidation as at the start, and no other volatile constituent is present, does the loss in weight upon treatment with hydrofluoric and sulfuric acids represent the silica content. If the silicate is only partly decomposed with acid it should be treated as an insoluble silicate.

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[1] By being kept in contact with the acid for too long a time some silicic acid will go into solution.

[2] If the water is not added, the mass will effervesce so strongly that there is danger of losing some of the impure silica.

Determination of the Alkalies

Method of J. Lawrence Smith[1]

Principle. The substance is heated with a mixture of 1 part ammonium chloride and 8 parts calcium carbonate. By this means the alkalies are obtained in the form of chlorides, while the remaining metals are for the most part left behind as oxides (silicates and aluminates), and the silica is changed to calcium silicate, as represented by the following equations:

$$CaCO_3 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + H_2O + CO_2$$
$$2KAlSi_3O_8 + CaCl_2 + 6CaCO_3 \rightarrow 6CaSiO_3 + Ca(AlO_2)_2 + 2KCl + 6CO_2$$

The alkali chlorides together with the excess calcium chloride can be removed from the sintered mass by leaching with water, while the other constituents remain undissolved.

Preparation. The ammonium chloride necessary for the determination is prepared by subliming the commercial salt; the calcium carbonate by dissolving the purest calcite obtainable in hydrochloric acid and precipitating with ammonia and ammonium carbonate. Carry out this last operation in a large porcelain dish. After the precipitate has settled, pour off the clear solution and wash the precipitate by decantation until free from chlorides. The product thus obtained contains traces of alkalies, but the amount present can be determined once for all by a blank test and a corresponding deduction made from the results of the analysis; it is usually sodium chloride and amounts to 0.0012–0.0016 g for 8 g calcium carbonate. The decomposition was performed by Smith in a finger-shaped crucible about 8 cm long and with a diameter of about 2 cm at the top and 1½ cm at the bottom. Such a crucible is suitable for the decomposition of about 0.5 g of the mineral. A larger quantity can be analyzed in a somewhat wider crucible.

Filling the Crucible. Mix 0.5 g of the mineral (accurately weighed) with an equal quantity of sublimed ammonium chloride by trituration in an agate mortar, add 3 g of calcium carbonate, and intimately mix again. Transfer the mixture to a platinum crucible with the help of a piece of glazed paper, rinse the mortar with 1 g of calcium carbonate, and add this to the contents of the crucible.

The Ignition. Place the covered crucible in a slightly inclined position and heat gradually over a small flame until no more ammonia is evolved (this should take about 15 minutes). During this part of the operation the heat should be kept so low that ammonium chloride does not escape. The latter is dissociated into ammonia and hydrochloric acid by the heat, and the acid unites with the calcium carbonate to form calcium chloride. It is possible to decompose the silicate by using calcium chloride alone. Gradually raise the temperature until finally the lower three-fourths (and no more) of the crucible is brought to a dull red heat, and maintain this temperature for 50–60 minutes. Then allow the crucible to cool; the sintered cake usually can be removed by gently tapping the inverted crucible. If it cannot, digest a few minutes with water, which serves to soften the cake so that it can be readily washed into a large porcelain, or, better, platinum dish. Heat the covered dish with 50–75 ml of water for half an hour, replacing the water lost by evaporation and reducing the larger particles to a fine powder by rubbing with a pestle in the dish. Decant the clear solution through a filter and wash the residue 4 times by decantation, then transfer to the filter and wash with hot water until a few milliliters of the washings give only a slight turbidity with silver nitrate. To make sure that the decomposition of the mineral has been complete, treat the residue with hydrochloric acid; it should decompose completely, leaving no trace of undecomposed mineral. The acid usually gelatinizes silica; the formation of a gelatinous precipitate does not indicate incomplete decomposition.

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[1] *Am. J. Sci.* [2], **50,** 269, and *Ann. Chem. Pharm.*, **159,** 82 (1871).

Precipitation of the Calcium. To the aqueous solution add 50 ml of ammonium carbonate reagent, heat nearly to boiling, and filter. Evaporate the filtrate to dryness in a porcelain or platinum dish, heat the contents of the dish for an hour in a drying oven at 110°, and remove ammonium salts by careful ignition over a moving flame. After cooling, dissolve the residue in a little water and remove the last traces of calcium by the addition of ammonia and ammonium oxalate to the hot solution. After standing 12 hours, filter off the calcium oxalate and receive the filtrate in a weighed platinum dish, evaporate to dryness, and gently ignite. After cooling, moisten the mass with hydrochloric acid to transform any carbonate into chloride, repeat the evaporation and ignition, and determine the weight of the dish and its contents; this shows the amount of alkali chloride present.

Separation of Sodium and Potassium

The separation of the alkali cations from one another is somewhat of a problem because most salts of the alkalies are fairly soluble in water. The elements lithium, rubidium, and cesium are not present in common minerals to an appreciable extent so that ordinarily the chemist is concerned chiefly with the determination of only sodium and potassium. In general, it may be stated that the compounds of rubidium and cesium resemble those of potassium, and when a potassium salt is less soluble than the corresponding sodium salt, the rubidium salt will be still less soluble and the cesium salt least soluble of all. The relationship between increasing atomic weight and solubility helps one to remember the relative solubilities.

The salts of potassium which are distinctly less soluble than the corresponding sodium salts, and which have been proposed for the identification and determination of potassium ions, are the chloroplatinate, K_2PtCl_6, the perchlorate, $KClO_4$, the cobaltinitrite, $K_2NaCo(NO_2)_6$, the acid tartrate (cream of tartar), $KHC_4H_4O_6$, and the double sulfate with zirconium, $2ZrO_2 \cdot K_2O \cdot (SO_3)_2$. The first of these compounds, potassium chloroplatinate, is practically insoluble in alcohol whereas the anhydrous sodium chloroplatinate dissolves in alcohol. By adding sufficient chloroplatinic acid, H_2PtCl_6, to combine with both the sodium and potassium and evaporating to dryness, it is possible to convert a mixture of sodium and potassium chlorides into one of chloroplatinates and then the sodium chloroplatinate can be dissolved in alcohol leaving behind the potassium chloroplatinate which can be dried and weighed. This method is perhaps the oldest and best known for separating sodium and potassium. It is still widely used but is costly, owing to the high price of platinum and the time required to recover this element from the precipitates and mother liquors. Moreover, the composition of the precipitate does not always correspond exactly to the formula, K_2PtCl_6. The method is not so accurate as is sometimes assumed.

The separation by means of sodium cobaltinitrite reagent has received considerable attention in the literature. The precipitate of potassium cobaltinitrite is much less soluble than potassium chloroplatinate, it can be weighed as $K_2NaCo(NO_2)_6$, the cobalt content can be determined electrolytically or the nitrite content by oxidation with permanganate. The cobaltinitrite method for separating potassium and sodium was recommended by de Koninck,[1] and since then many chemists have testified to its usefulness. The reagent, however, is not very stable, and the composition of the precipitate is not always the same.

The precipitation of potassium by zirconium sulfate in a concentrated, neutral, aqueous solution has been recommended; it furnishes a means of separating sodium and potassium which is a promising one. According to Reed and Withrow[2] the precipitation of potassium can take place in the presence of sodium, ammonium, lithium, rubidium, and cesium ions, but this statement is contradicted by Yajnik and Tandon,[3] who have found it possible to precipitate rubidium and cesium quantitatively by means of zirconium sulfate in a neutral solution.

A method often used for estimating the sodium and potassium content in a weighed portion of their chlorides is to determine the chloride content by titration with silver nitrate solution or by adding a measured volume of silver solution and titrating the excess silver with thiocyanate solution (cf. p. 148). This method is rapid but not altogether satisfactory because the chloride content of potassium chloride does not differ sufficiently from that of sodium chloride; any error in the titration is multiplied nearly eightfold in estimating the composition of the original mixture.

Probably the most reliable method for analyzing a mixture of sodium and potassium chlorides is the modification of the perchlorate method which has been worked out by H. H. Willard[4] and his associates. The mixture of chlorides is converted into one of perchlorates by evaporation with perchloric acid, the sodium perchlorate is extracted with a mixture of *n*-butyl alcohol and ethyl acetate, and the potassium perchlorate dried and weighed. The sodium content can be determined from the original weight of the mixture after deducting a weight of potassium chloride equivalent to that of the potassium perchlorate found, or the filtrate from the potassium perchlorate precipitate can be evaporated to remove the ethyl acetate and the sodium precipitated as chloride by adding a solution of hydrogen chloride in butyl alcohol.

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[1] *Z. anal. Chem.*, **20**, 390 (1881).

[2] *J. Am. Chem. Soc.*, **51**, 1062 (1929).

[3] *J. Indian Chem. Soc.*, **7**, 287–96 (1930).

[4] Willard and Smith, *J. Am. Chem. Soc.*, **44**, 2816 (1922); G. F. Smith, *ibid.*, **47**, 762 (1925); Smith and Ross, *ibid.*, **47**, 774, 1020 (1925); Willard and Smith, *ibid.*, **45**, 293 (1923).

Procedure. If the solution to be analyzed contains sulfate, it is advisable to remove it. To about 70 ml of solution (containing not more than 0.5 g of potassium salt) add 1 ml of concentrated hydrochloric acid heat to a gentle boil, and add hot 0.5 *N* barium chloride solution drop by drop until no further precipitation occurs. Wait 15 minutes; filter off the barium sulfate and wash it with hot water.

If ammonium salts are present, evaporate to dryness in a porcelain dish and ignite carefully till all ammonium salts are decomposed. Cool, rinse down the sides of the dish with a little water, again evaporate, and ignite at a temperature below redness. Dissolve the residue in about 20 ml of water and transfer to a 150-ml Pyrex beaker.

To the solution of chlorides add 2 or 3 times as much of 9 *N* perchloric acid as is theoretically necessary to convert the chlorides to perchlorates (not less than 1 ml in any case). Evaporate to dryness on the hot plate, at a temperature not exceeding 350°, and expel any acid condensed on the side walls of the beaker by playing a free flame against the outside. Cool, wash down the sides of the beaker with 3 to 5 ml of hot water, and again evaporate to dryness on the hot plate. Cool; add 10 to 20 ml of a mixture of equal parts by volume of *n*-butyl alcohol and ethyl acetate. Digest on the steam bath[1] for 2 or 3 minutes and then cool to room temperature.

Decant the liquid through a previously ignited and weighed filtering crucible and wash the precipitate 3 times by decantation with 5-ml portions of the alcohol-acetate mixture. Reserve the filtrate and washings if it is desired to make a direct determination of sodium.

Dissolve the residue in the crucible with a very little hot water, catching the solution in the original beaker. Again evaporate to dryness. Add 10 ml of the butyl alcohol-acetate mixture; digest and cool as before. Filter through the original crucible, which has been dried meanwhile. Transfer the precipitate to the crucible and wash 10 to 15 times with less than 1-ml portions of the alcohol-acetate mixture. Dry the beaker and brush any particles of potassium perchlorate into the crucible. Dry an hour at 110° and 15 minutes at 350°. Cool and weigh as $KClO_4$.

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[1] Be careful not to use a free flame because if the combustible vapors catch fire a dangerous explosion will result.

To determine the sodium, evaporate the combined filtrates and washings till the volume is not over 20 ml at the most and all the ethyl acetate has been removed. Heat to 80 to 90°, and add dropwise, with stirring, 2 ml of a 20 per cent solution of hydrogen chloride in *n*-butyl alcohol (prepared by passing dry hydrogen chloride into 200 ml of butyl alcohol for 2 hours; the density of the solution is 0.905). Then add 6 ml more of the HCl-alcohol solution, cool to room temperature, filter off the precipitated sodium chloride, and wash 8 or 10 times with 1-ml portions of 6 to 7 per cent solution of hydrogen chloride in butyl alcohol. Dry 15 minutes at 110° and then for 5 minutes at 600°. Cool and weigh as NaCl or dissolve the salt in water and titrate the chloride (see p. 148).

HOME PROBLEMS

1. A silicate weighing 1.47 g yielded 0.685 g of Fe_2O_3 and Al_2O_3. This residue was digested with a little 3 *N* HCl until dissolved and the solution treated with exactly 60 ml of 0.125 *N* $SnCl_2$. The excess of $SnCl_2$ reacted with 8 ml of iodine solution. Forty milliliters of the I_2 solution is equivalent as oxidizing agent to the permanganate required to oxidize 60 ml of K tetroxalate solution which is 0.1 *N* as an acid. Find the percentage of FeO and Al_2O_3 in the mineral, assuming all Fe to be originally in the ferrous state.

2. A sample of Cu ore carrying metallic Cu was prepared by crushing 94 g until all but 9.23 g has passed through a 120-mesh sieve. The residue on the sieve contained 93.2 per cent Cu, and the powder assayed 20.38 per cent Cu. Find the percentage of Cu in the ore.

3. What volume of 6 *N* H_2F_2 is absolutely necessary for the volatilization of all the Si in 0.68 g of pure feldspar, $KAlSi_3O_8$? What volume of SiF_4 measured at 24°C and 745 mm pressure is produced?

4. What is the empirical formula of a mineral containing 3.37 per cent H_2O, 19.10 per cent Al_2O_3, 21.0 per cent CaO, and 56.35 per cent SiO_2?

Which of the following symbols of other silicates are possibly correct: $Be_3Al_2(SiO_3)_6$; $HCa_3BAl_2Si_4O_{16}$; $HCa_2Al_3Si_3O_{16}$; $H_4SrAl_2Si_6O_{17}$?

5. Using 0.500 g of pure $NaKCaSi_3O_8$, what would be the cost of the perchloric acid at $18 per liter for 3 *N* $HClO_4$, assuming that 5 per cent more is added than is necessary to combine with both Na and K? Find the cost of Pt at 80¢ per gram, required to give sufficient $H_2PtCl_6 \cdot 6H_2O$ to react similarly with the same assumptions. Assuming that 50 such analyses are to be made, how much would be saved by using the cheaper reagent?

6. On the basis that no atom is united directly with another of the same kind, write possible structural symbols for sulfuric acid, sodium pyrosulfate, borax, $Be_3Al_2(SiO_3)_6$, sodium hypophosphite, and sodium pyrophosphate.

7. A mineral contains 4.36 per cent H_2O, 27.13 per cent CaO, 24.69 per cent Al_2O_3, and 43.82 per cent SiO_2. Compute the empirical formula, and write a structural symbol for it.

8. From 0.5 g of feldspar, a mixture of pure NaCl and KCl weighing 0.15 g and containing 55 per cent Cl was obtained. Compute the percentage of K_2O and of Na_2O and the weight of K_2PtCl_6 which could be obtained from the KCl by precipitation with H_2PtCl_6.

9. From 0.48 g of a mixture of pure NaCl, KCl, and LiCl, which in turn was prepared from 1.600 g of a silicate, a solution was obtained which contained chloride equivalent to 90 ml of ninth-normal $AgNO_3$ and K equivalent to 0.1052 g K_2PtCl_6. Compute the percentage of Na_2O, K_2O, and Li_2O in the silicate.

CHAPTER XV

DETERMINATION OF PHOSPHORUS IN STEEL

Phosphorus is present in all kinds of iron and steel as well as in the various alloys used in steel-making. In general, it is detrimental, and the permissible quantities are usually defined rigidly in specifications of material. Phosphorus is sometimes added intentionally in the manufacture of sheet steel to prevent the sheets from sticking together during the rolling process.

The phosphorus content of most steels lies between 0.01 and 0.1 per cent; ingot iron contains less than 0.01 per cent, and wrought iron usually between 0.1 and 0.2 per cent. In most steels it exists as a solid solution of iron phosphide, Fe_3P, in iron; but in many samples of cast iron, free iron phosphide is found. In wrought iron and in some low-carbon Bessemer steels it is possible that a little phosphate may exist.

The presence of too much phosphorus in steel causes brittleness; the metal is likely to break when subjected to sudden stress.

All methods for determining phosphorus in iron and steel are based upon the preliminary oxidation of the phosphorus to phosphoric acid. Practically all phosphates except those of the alkali metals are insoluble in water, but the phosphoric acid obtained in the chemical examination of iron and steel is usually precipitated first as ammonium phosphomolybdate or as ferric phosphate.

The gravimetric methods are based upon the separation of the phosphoric acid from at least the greater part of the iron by precipitation either as ammonium phosphomolybdate or as ferric phosphate; in the latter case the greater part of the iron is reduced to the ferrous condition after the complete oxidation of the phosphorus and enough is left in the ferric condition so that in carrying out a basic acetate separation all the phosphorus is precipitated as ferric phosphate and the excess ferric iron as basic ferric acetate. From his study of qualitative analysis, the student is already familiar with this method of separating phosphate from bivalent cations. The basic ferric acetate precipitate can be dissolved in dilute hydrochloric acid, and the precipitation of ferric hydroxide or of ferric phosphate by neutralization with ammonia can be prevented by adding considerable citric or tartaric acid. Then on adding " magnesia mixture " to the ammoniacal solution (cf. p. 205) a precipitation of magnesium ammonium phosphate can be obtained. This method of analysis has been recommended but today is seldom used because it is tedious and yields no better results than other, more convenient procedures.

To separate a small quantity of phosphoric acid from a large quantity of iron, it is customary to precipitate the former as ammonium phosphomolybdate by adding ammonium molybdate reagent to the nitric acid solution. The yellow precipitate is least soluble in dilute acids containing considerable dissolved salt. The dry precipitate weighs about 61 times as much as the phosphorus it contains, as is evident from its formula, which is usually written $(NH_4)_3PO_4 \cdot 12MoO_3$. The student who has determined the phosphorus content of apatite (cf. p. 204) already knows how the phosphorus of yellow ammonium phosphomolybdate can be converted into magnesium ammonium phosphate. Even today this method of analysis is applied to the determination of phosphorus in steel in " umpire analyses " to settle disputes among chemists. Many years of experience have shown that the so-called " rapid methods " are just as accurate as the longer methods when properly carried out, but they are sensitive to slight changes in the conditions such as the temperature, time allowed for the completion of the reaction, concentration, and acidity. Rapid methods are sometimes based on the weight or volume of the ammonium molybdate precipitate. Thus the precipitate is sometimes weighed after drying a definite time at a definite temperature and at other times its volume is read after centrifuging in a graduated tube.

The rapid methods to be described here are based upon the determination of the molybdenum content from which the phosphorus can be computed on the assumption that the precipitate contains 12 atoms of molybdenum to 1 atom of phosphorus. The molybdenum content can be estimated by measuring the volume of a standardized solution of sodium hydroxide required to dissolve the precipitate. This is accomplished by dissolving the precipitate in a measured volume of the alkali hydroxide solution and determining the excess by titrating to a phenolphthalein end point with standard acid. Another method of estimating the molybdenum content is to reduce the molybdate solution with zinc in the presence of acid and then measure the volume of standard potassium permanganate solution required to oxidize the molybdenum back to the valence of 6. Some chemists prefer to convert the molybdenum to lead molybdate and weigh it. The weight of the lead molybdate precipitate is 142 times as great as the equivalent weight of phosphorus in this method of analysis.

In this book three rapid methods of analysis will be described, each of which depends upon oxidizing the phosphorus to phosphoric acid and precipitating it as ammonium phosphomolybdate. The sample of steel is dissolved in 4 *N* nitric acid (sp. gr. = 1.135). As a general rule, the steel dissolves easily in acid of this concentration, and there is no danger of losing phosphine. The reaction between iron phosphide and hot, dilute nitric acid can be expressed as follows:

$$3Fe_3P + 41H^+ + 14NO_3^- = 9Fe^{+++} + 3H_3PO_4 + 14NO + 16H_2O$$

which means that 41 molecules of HNO_3 are required to dissolve 1 molecule of Fe_3P but only 14 molecules of the NO_3^- are reduced to NO.

The easiest way to balance such an equation is to consider first the relation between the substance oxidized and the one reduced. We notice at once that Fe_3P does not correspond to any ordinary salt of iron, and we can say that Fe_3P represents a *neutral* molecule without bothering at all about the valence of the Fe or of the P. When it is dissolved and oxidized by HNO_3, ferric nitrate and phosphoric acid are formed, and in these compounds the Fe has a positive valence of 3 and the phosphorus a positive valence of 5. (The old-fashioned way was to say that the Fe was oxidized to the state represented by Fe_2O_3 and the P to the state represented by P_2O_5, but this means exactly the same thing.)

The neutral molecule of Fe_3P, therefore, accepts $9 + 5 = 14$ positive charges. The HNO_3, on the other hand, is reduced to NO, and the atom of N loses 3 positive charges. In this way the numbers 14 and 3 are obtained in the above equation. Then, if the equation is written out as far as we have gone, we see that we have 27 positive charges on the right, and this number, added to the 14 charges necessary to neutralize the 14 negative charges of the NO_3^- anion, makes $41H^+$ required on the left-hand side of the equation. The equation shows that 41 moles of HNO_3 are required to dissolve 3 moles of Fe_3P, but of these 41 moles, only 14 are reduced to NO and the remaining 27 moles are left as $9Fe(NO_3)_3$.

When steel dissolves in nitric acid, a small carbide residue usually remains. The carbide may dissolve and exert a reducing effect at some stage in the analysis. It is best, therefore, to make sure that the carbide is thoroughly oxidized. This can be accomplished by evaporating the solution to dryness and baking the residue, which is then hard to get back into solution. It is much more expeditious to add some strong permanganate to the original nitric acid solution; after this treatment the phosphorus will surely have been oxidized to its highest state of valence.

In the three methods to be described, the procedure will be the same, down to the precipitation of the phosphorus as ammonium phosphomolybdate (cf. p. 204).

$$12MoO_4^{--} + H_3PO_4 + 21H^+ + 3NH_4^+ \rightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 12H_2O$$

Reagents Required. The most important reagent is the ammonium molybdate solution. For the last fifty years, the reagent most used in the United States is a solution containing, besides the ammonium molybdate, considerable ammonium nitrate and free nitric acid. When this reagent is used, the solution analyzed should be nearly neutral as sufficient nitric acid is present in the reagent to provide for complete precipitation, but if the solution to be analyzed contains considerable free acid or if it is basic in reaction the precipitation of the phosphoric acid will be incomplete. The acid molybdate reagent, however, is not very stable and stains the fingers if spilled upon them. For that reason, many chemists prefer to use a neutral or slightly ammoniacal solution of ammonium molybdate. Three formulas for preparing the reagent will be given. The first is the reagent recommended by Blair which is strongly acidic and, according to chemists of the National Bureau of Standards, is still most used. It has been used at the Massachusetts Institute of Technology for over forty years. The second formula has been recommended by the American Society of Testing Materials; it is similar to the third formula, which is recommended by C. M. Johnson.

Personally, the writer prefers the third formula, but some of his colleagues like the first one, and experience has shown that confusion will result if the stockroom uses more than one formula. In carrying out this analysis, the student should find out which formula comes nearest to that used in the laboratory in which he is working.

Acid Ammonium Molybdate Solution. Mix 100 g of pure MoO_3, or 118 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (85 per cent MoO_3), with 400 ml of water, and dissolve it in 80 ml of strong NH_4OH (d 0.90 or about 15 N) with stirring. Filter if necessary, cool and pour very slowly, while stirring, into 715 ml of 6 N HNO_3. Add 1 or 2 drops of 10 per cent NH_4HPO_4 solution and allow to stand at least 12 hours. Decant off the clear liquid or filter through an asbestos pad as required for use.

Ammonium Molybdate (A.S.T.M. Formula). Take 65 g of pure $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 225 g of NH_4NO_3, 15 ml of concentrated NH_4OH, and 600 ml of water. Stir and heat gently. When the crystals have dissolved, filter (without washing) and dilute to 1 l.

Ammonium Molybdate (Johnson's Formula). Digest 55 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and 50 g of NH_4NO_3 with 18 ml of 15 N NH_4OH and 20 ml of water. Stir, dilute to about 700 ml with water, and heat for 30 minutes with occasional stirring until all salts have dissolved. Dilute to 1 l, let stand over night, filter, but do not wash the residue.

Standard Sodium Hydroxide. Dissolve 6.6 g of NaOH pellets in water, dilute to 1 l, add 1 ml of saturated $Ba(OH)_2 \cdot 8H_2O$ solution, and store in a bottle with a CO_2 trap containing Ascarite (cf. p. 74). Standardize the solution against about 0.6 g of $KHC_8H_4O_4$, weighed to the nearest 0.1 mg, with phenolphthalein as indicator (cf. p. 73).

Standard HNO_3. Dilute 7 ml of concentrated HNO_3 or 20 ml of 6 *N* HNO_3 to 1 l. Standardize against the NaOH solution by measuring out accurately 25 ml of the acid, diluting with 25 ml of CO_2-free water, adding 2 drops of phenolphthalein indicator, and titrating with the NaOH. If many analyses for phosphorus are to be performed, it is convenient to make 1 ml of each of the two solutions exactly equivalent to 0.0002 g P (1 P = 23 NaOH); then, with a 2-g sample of steel, 1 ml = 0.01 per cent P. Such a solution is 0.1483 *N*.

Tenth-Normal Permanganate. See p. 110.

Ferric Alum. Moisten 100 g of ferric alum $(Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ with 25 ml of concentrated H_2SO_4 and 40 ml of 85 per cent H_3PO_4 (about 15 *N*). Dilute carefully to 1 l.

Nitric Acid for Dissolving. It is usually recommended that HNO_3 *d* 1.135, be used for dissolving the sample of steel. This acid is strong enough to prevent loss of phosphine and does not cause gelatinization of silicic acid as readily as stronger acid does. To prepare it, mix 140 ml of concentrated HNO_3, *d* 1.42, with 360 ml of water. The solution is approximately 4 *N*. Chemists of the U. S. Steel Corporation, in their *Directions*, revised to 1937, now recommend the 6 *N* HNO_3.

Procedure for Carbon Steels and Alloy Steels Soluble in Nitric Acid. Use of Acid Ammonium Molybdate Reagent

Plain Carbon Steel. Weigh 2 g of steel to the nearest centigram into a 300-ml Erlenmeyer flask, add 100 ml of approximately 4 *N* nitric acid (see above), and insert a small, short-stemmed funnel into the neck of the flask. Heat until the sample is entirely dissolved and very little oxide of nitrogen is visible in the neck of the flask. Add 10 ml of 1.5 per cent $KMnO_4$ solution and boil gently for 2 to 3 minutes. The purpose of the permanganate is to oxidize the dissolved carbide and to make sure that all the phosphorus is fully oxidized to phosphoric acid. If no precipitate appears, add more permanganate and boil again. Dissolve the precipitate of MnO_2, and reduce the excess $KMnO_4$ by adding a few drops of sulfurous acid, a small crystal of ferrous sulfate, or some 5 per cent sodium thiosulfate solution. Add very little of the reducing agent at a time, but continue adding it, at short intervals, until the manganese dioxide is dissolved. If there is any appreciable silicious residue at this point it should be removed by filtration. Boil 2 minutes after the manganese dioxide has dissolved, and then cool to 40°. If the volume of the solution is less than about 80 ml at this stage of the analysis, more 4 *N* nitric acid should be added. Add 40 ml of 6 *N* ammonium hydroxide in portions of 25, 10, and 5 ml, and rotate the flask until the precipitated ferric hydroxide redissolves. It is important that the solution should now assume a pale straw color and not appear at all red from colloidal ferric hydroxide. A red solution shows that too much ammonia was added and more nitric acid must be added or the precipitation of the phosphorus will be incomplete. With the solution at about 40° add 40 ml of the acid ammonium molybdate solution. Stopper the flask with a rubber stopper and shake vigorously for 5 minutes; allow the precipitate to settle for 15 minutes but in no case over half an hour.

From this point, the procedures vary. In the alkalimetric method, the volume of sodium hydroxide required to dissolve the precipitate is determined; in the oxidimetric method, the volume of permanganate solution required to react with the molybdenum after its reduction is measured; and in the lead molybdate method, the molybdenum is weighed as lead molybdate.

Alternative Procedure. Use of Ammoniacal Ammonium Molybdate Reagent[1]

Treat 2 g of steel in a 300-ml Erlenmeyer flask with 50 ml of 6 *N* HNO_3. When the sample has dissolved add a slight excess of 2.5 per cent $KMnO_4$ solution (3–10 ml) to complete the oxidation. An excess is shown by the formation of MnO_2 precipitate or a persistent permanganate color. Dissolve the precipitate and reduce the excess permanganate by adding a few drops of sulfurous acid, sodium sulfite, or alkali nitrite, and boil to expel oxides of nitrogen and sulfur. Cool to about 70° and add 50 ml of ammonium molybdate prepared according to Johnson or to the A.S.T.M. formula (see p. 249). Stopper the flask, shake vigorously for 10 minutes, preferably mechanically, cool to 20° or below, and filter.

Procedure for Other Iron Alloys

Cast Iron. Dissolve 0.5–1 g of sample in half the quantity of HNO_3 recommended above, but after the oxidation with $KMnO_4$ filter through paper.

Nickel, Chrome-Nickel, Stainless, and Similar Alloy Steels Containing neither Tungsten nor Vanadium. If the sample does not dissolve in dilute nitric acid, treat 2 g of steel with 50 ml of a mixture of equal parts concentrated nitric and concentrated hydrochloric acids, and to the solution add 20 ml of concentrated $HClO_4$ (48 per cent $HClO_4 = 27\ N$). Evaporate to fumes of $HClO_4$ and continue heating 5 minutes to oxidize Cr to chromic acid and to dehydrate any silica. Cool somewhat, add 40 ml of water, filter, and wash with cold water.

Add dropwise a saturated solution of SO_2 until all the chromium and vanadium are reduced, and boil until the excess SO_2 is expelled. With the filtrate at about 90°, add 50 ml of either of the slightly ammoniacal ammonium molybdate reagents and shake well for 5 minutes. Filter and wash in the usual manner.

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[1] *Sampling and Analysis of Carbon and Alloy Steels.* Methods of the Chemists of the United States Steel Corporation as Revised to 1937.

High-Speed Steels or Other Steels Containing Tungsten and Vanadium. Treat 3 g of steel with 60 ml of 4 *N* HNO_3. Add 30 ml of concentrated HCl and evaporate to dryness. Take up the residue in 20 ml of 6 *N* HCl with gentle heating. Dilute to 100 ml with hot water and filter off the WO_3. Evaporate the filtrate twice with 20-ml portions of concentrated HNO_3 to expel the HCl, but be careful not to bake the residue. Carry the second evaporation to the point where the residue is sirupy, add 100 ml of 4 *N* HNO_3, and filter. Wash the residue with cold water, and neutralize with 40 ml of 6 *N* NH_4OH. Cool the solution to 15°; add 5 ml of approximately 1.5 *N* ferrous sulfate solution (400 g $FeSO_4 \cdot 7H_2O$ per liter) to reduce the vanadic acid and 2–3 drops of saturated sulfurous acid. Add 75 ml of the *acid* ammonium molybdate reagent, shake for 10 minutes, and allow to stand 4 hours or more before filtering off the yellow ammonium phosphomolybdate precipitate.

In the above directions and throughout the book concentrated nitric acid refers to the 16 *N* acid of density 1.42 and concentrated hydrochloric acid to the 12 *N* acid of density 1.2.

Alkalimetric Method

Filter off the precipitate and use a 9-cm ashless filter paper that fits the funnel tightly. Wash the flask, precipitate, and paper twice with 5-ml portions of 1 per cent HNO_3 (1 ml concentrated acid to 100 ml of water) and then 5 times with 5-ml portions of 1 per cent KNO_3 solution. Finally wash the paper with cold 1 per cent KNO_3 until 10 ml of the last filtrate will not decolorize 1 drop (0.03 ml) of 0.1 *N* NaOH and 1 drop of phenolphthalein indicator solution. This usually requires about 10 washings more than are specified above. Direct the dilute KNO_3 solution around the edge of the filter and then spirally down, and wait until the liquid has drained before washing again.

Return the paper and the precipitate to the Erlenmeyer flask in which the precipitation took place, add 25 ml of water, 3 drops of phenolphthalein indicator solution, and, from a buret or pipet, 10 ml of 0.1 *N* NaOH free from carbonate. This will usually be sufficient to dissolve all the yellow precipitate and leave the solution alkaline to phenolphthalein. If necessary add more NaOH. Discharge the pink color by adding a measured volume of 0.1 *N* HNO_3 from a buret, and finish the titration by adding just enough more of the 0.1 *N* NaOH to impart a pink color to the solution.

The chemical equation that represents the dissolving of the precipitate, with the solution left neutral to phenolphthalein (cf. p. 59), is the following

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 23OH^- \rightarrow 12MoO_4^{--} + 3NH_4^+ + HPO_4^{--} + 11H_2O$$

From this equation it is clear that

$$1P \approx 12Mo \approx 23OH^-$$

and the milliequivalent weight of phosphorus by this method of analysis is P/23,000 = 0.001349 g of phosphorus.

Oxidimetric Method

Transfer the yellow precipitate to a paper filter in the same way as in the above method but, instead of the 1 per cent HNO_3 and 1 per cent KNO_3 solutions, use an acid ammonium sulfate solution (1 l of water, 25 ml concentrated H_2SO_4, and 15 ml strong ammonia; mix well before using). Wash the precipitate promptly with ten 5-ml portions of this acid sulfate solution, wetting the upper edge of the filter paper each time and allowing each portion to drain through the filter paper before adding the next.

Dissolve the ammonium phosphomolybdate precipitate in 25 ml of 3 *N* ammonium hydroxide, wash the filter with hot water, and treat the filtrate with 10 ml of concentrated sulfuric acid. It is now ready for reduction with the Jones' reductor (see p. 115). Run a blank with the reductor before each series of determinations and whenever the reductor has stood idle for 3 hours. After a reductor has stood over night, it should be well washed with dilute sulfuric acid, before even a blank test is run. Titrate the reduced solution with permanganate.

In making blanks and in all determinations, the procedure is as follows. Add 100 ml of normal sulfuric acid through the funnel, *B*, with the stopcock *C* open, using a little suction. When only a little of the dilute acid remains in the funnel, add the solution to be reduced or, for blanks, 50 ml of 1.5 *N* sulfuric acid, and when this has nearly passed out of the funnel, follow with 250 ml of normal sulfuric acid, washing out the original beaker with this acid and adding it in small portions. Finally, pass 100 ml of water through the reductor and titrate in the permanganate. Air should not be allowed to enter the reductor tube, which should be kept full of water at all times when idle. Run blanks until two successive tests require less than 0.2 ml of 0.1 *N* permanganate to give a pink color to the acid solution.

In the original method, the reduced solution was caught in an empty flask and it was assumed that the MoO_3 of the phosphomolybdate precipitate was reduced to $Mo_{24}O_{37}$; 1 ml of 0.1 *N* $KMnO_4$ = 0.0000886 g P. The molybdenum is reduced completely to the trivalent condition by the amalgamated zinc:

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 23NH_4OH = 12(NH_4)_2MoO_4 + (NH_4)_2HPO_4 + 11H_2O$$
$$2MoO_4^{--} + 3Zn + 16H^+ \rightarrow 2Mo^{+++} + 3Zn^{++} + 8H_2O$$

The trivalent molybdenum is slowly oxidized by the air in the flask and by that shaken into the solution during the titration. A practiced manipulator usually titrates so that about 3 per cent of the total oxidation is accomplished by the air, and this corresponds to the assumption that Blair made with respect to the hypothetical $Mo_{24}O_{37}$. The only safe way to avoid this error is to catch the reduced solution, before it comes in contact with air, in 50 ml of 10 per cent ferric alum solution (100 g of ferric alum, 25 ml of concentrated sulfuric acid, and 40 ml of sirupy phosphoric acid per liter).

This ferric alum solution does not change the reduced molybdenum entirely back to the 6-valent condition but it does oxidize it sufficiently to prevent the effect of the atmosphere, and for every equivalent of molybdenum oxidized an equivalent of reduced iron is formed so that the solution titrates exactly as if a perfect reduction was obtained without the use of the ferric salt. Since the precipitate contains 1P:12Mo, and the valence change of the Mo is 3, it is clear how the normal weight is computed. When this ferric alum solution is used in the analysis, it must be present also in running the blanks.

To illustrate the computation assume that the ammonium phosphomolybdate precipitate from 2 g of steel required by the above method 12 ml of 0.1 *N* permanganate solution. The blank on the reductor and ferric alum was 0.18 ml. The phosphorus present in the steel is then: $(12 - 0.18) \times 0.00431$ per cent.

If 2.16 g of steel is taken for analysis, the percentage of phosphorus will be 0.004 times the net volume of 0.1 *N* permanganate in milliliters when ferric alum is used.

Lead Molybdate Method

Filter the ammonium phosphomolybdate precipitate (see p. 251) and wash it on a 9-cm ashless filter paper with cold 1 per cent nitric acid (1 ml concentrated acid and 100 ml water) at least 10 times. Dissolve the precipitate by pouring 4 ml of concentrated NH_4OH on the filter. Catch the solution in the flask used for the precipitation, wash the paper once with hot water, and again pour this solution through the filter, this time catching it in a 150-ml beaker. Wash the paper at least 6 times with a stream of hot water directed against the upper edge of the paper and then place the solution on a hot plate. Place beside it a 250-ml beaker containing a filtered solution of 10 g NH_4Cl and 12.5 g of ammonium acetate in 50 ml of water. When both solutions are at the boiling point, add, to the ammoniacal solution of the yellow precipitate, 10 ml of concentrated hydrochloric acid and 10 ml of 4 per cent lead acetate solution. At once pour this mixture into the hot solution of ammonium chloride and acetate, and wash out the beaker with hot water. Allow the precipitate to settle for a few minutes and then filter through a weighed Gooch crucible. Wash thoroughly with hot water until free from chloride, dry in the hot closet at 105°, and weigh. If preferred, finish the washing with alcohol and ether (cf. p. 192).

In this method of analysis, $12PbMoO_4$ are obtained for each P present. The weight of phosphorus, therefore, is found by the formula:

$$\text{wt. ppt.} \times \frac{P}{12PbMoO_4} = \text{wt. ppt.} \times \frac{31.02}{4407} = \text{wt. ppt.} \times 0.00704$$

HOME PROBLEMS

10. A 2-g sample of steel containing 0.007 per cent P would require what net volume of $N/20$ $KMnO_4$ (*a*) if the molybdenum is reduced to a valency corresponding to $Mo_{24}O_{37}$; (*b*) if, with the aid of ferric alum, the oxidation corresponds to that of Mo^{+++} to H_2MoO_4. (*c*) What net volume of $N/14$ NaOH in the alkalimetric method? What would be the weight of the yellow precipitate if dried in a Gooch crucible until it becomes anhydrous?

11. Calculate the percentage of phosphorus in a sample of steel from the following data: 2.00 g of steel furnished a normal yellow precipitate which when dissolved and treated with Zn (see p. 253) reacted with 7.00 ml of $N/12$ $KMnO_4$.

12. Calculate the percentage of phosphorus in a steel from the following data: 2 g of steel furnished a yellow precipitate which was dissolved in 20.00 ml of half-normal sodium hydroxide solution and the excess of the latter reacted with 27.00 ml of third-normal nitric acid.

13. A normal yellow precipitate of ammonium phosphomolybdate from a sample of bronze weighing 1 g is reduced with zinc. The reduced solution requires 21.13 ml of $N/10$ permanganate to oxidize the molybdenum to the hexavalent condition. If the alloy contains exactly 0.2 per cent of phosphorus, to what oxide was the molybdenum apparently reduced by the zinc?

14. In the analysis of a sample of steel weighing 1.881 g, the phosphorus was precipitated with ammonium molybdate and the yellow precipitate was dissolved, reduced, and titrated with permanganate. If the sample contained 0.025 per cent P and 6.01 ml of $KMnO_4$ were used, to what oxide was the molybdenum reduced? One milliliter of $KMnO_4$ was equivalent to 0.007188 g of sodium oxalate.

15. In the analysis of apatite, 2.384 g of an *abnormal* yellow precipitate of ammonium phosphomolybdate was obtained, dissolved in 500 ml of ammonia water, and the solution mixed. Of this 50 ml was reduced by a certain reducing agent and then oxidized back to the valence of 6 with 30 ml of $N/10$ $KMnO_4$; 250 ml of the solution yielded 0.0852 g of $Mg_2P_2O_7$; and 100 ml gave 0.216 g of MoO_3. Find (*a*) ratio of P to Mo in the yellow precipitate; (*b*) symbol of the reduced oxide of Mo; (*c*) value of 1 ml of $KMnO_4$ in terms of P.

16. A sample of steel is analyzed by the alkalimetric method for phosphorus. In the analysis 15.0 ml of 0.08 N NaOH is added to dissolve the ammonium phosphomolybdate precipitate, and the excess is titrated with n milliliters of HNO_3. Find the weight of sample and the normality of the nitric acid when $(12 - n)/75 =$ per cent P.

17. In the analysis of 1.63 g of steel by the alkalimetric method, find the normalities of both the NaOH and the nitric acid when 15.0 ml of NaOH is used, n ml of HNO_3, and $(15 - 2n)/60 =$ per cent P.

18. In the determination of phosphorus in steel by the lead molybdate method, find the percentage of phosphorus when 0.120 g of $PbMoO_4$ is obtained from 2.05 g of steel.

CHAPTER XVI

MANGANESE IN STEEL

Manganese exists in ordinary steels as a solid solution with iron. Small quantities of manganese may be present as manganous sulfide or silicate, forming a part of the slag that is unintentionally left in the steel; breaks in the metal often start from such inclusions. Manganese, in the form of ferromanganese or "spiegeleisen," is introduced into molten steel for the purpose of deoxidizing and desulfurizing the metal and to prevent "red shortness" or brittleness during the forging heats. Some excess always appears in the finished steel, which ordinarily contains 0.2 to about 1.0 per cent. Manganese tends to increase the hardness and decreases somewhat the ductility of ordinary steels.

In metals containing more than 1 per cent of manganese, the hardness and brittleness increase rapidly, reaching maximums between 5 and 6 per cent, when it is practically impossible to machine the metal with any tool. Beyond 7 per cent of manganese causes progressive increase in the ductility, and steels containing 13 per cent manganese are very strong, tough, and ductile. The addition of manganese to steel lowers the transformation temperatures (see Carbon) and makes the transformations take place in a sluggish manner. Sometimes the Ar_1 point falls below the ordinary room temperature and self-hardening steels result.

Samples of iron or steel are usually dissolved in hot dilute nitric acid when manganese is to be determined. If tungsten is present, sulfuric acid is commonly used followed by nitric and sometimes phosphoric acid.

Usually it is not necessary to get rid of the iron before attempting to determine manganese because reactions typical of manganese can be made to take place in the presence of considerable quantities of ferric salt.

A fair separation of manganese from iron can be accomplished with ammonia and ammonium chloride, but when much iron and little manganese are present this method is rarely used; the precipitate of ferric hydroxide is very bulky and hard to handle, and the separation is never satisfactory with a single precipitation. The basic acetate separation, which depends upon the precipitation of basic ferric acetate, ferric phosphate, etc., by boiling the faintly acid solution with considerable sodium acetate, is better but also very tedious. More satisfactory is the treatment with an emulsion of zinc oxide and water. This serves to precipitate hydroxides which are more insoluble than zinc oxide. When this treatment is carried through it is customary to make up the solution and precipitate to a definite volume, mix well, and take a fraction (aliquot) of the filtered solution for the subsequent analysis. A slight error is introduced by the volume occupied by the precipitate, but the actual weight of the precipitate from 3 g of steel in 500 g of solution is relatively small, and the bulky ferric hydroxide precipitate tends to adsorb enough manganese to compensate for the fact that the actual volume of solution is somewhat less than 500 ml.

Two other methods of separating ferric and manganous ions are worth mentioning although it is rarely necessary to make use of them in the determination of manganese in steel. (1) If a small volume of ferric and manganous chlorides in hydrochloric acid solution (*d* 1.10) is shaken with a larger volume of ether, nearly all the ferric chloride, considerable hydrochloric acid, but no manganous chloride will pass into the ether layer. This is the Rothe ether separation, which has been much used in analytical chemistry. (2) If a dilute hydrochloric acid solution of ferric and manganous chlorides is treated with cupferron — the ammonium salt of phenylnitrosohydroxylamine, $C_6H_5(NO)NONH_4$ — ferric ions are precipitated as the salt of cupferron; in 3 cupferron molecules the NH_4 groups are replaced by Fe.

Practically all methods used for determining manganese in steel, or other ferrous alloys, are based upon the oxidation of bivalent manganous ions to some higher valency. In one method (Volhard's) the quantity of oxidizing agent ($KMnO_4$) required to accomplish the oxidation is measured, but in most methods the oxidized manganese is treated with a carefully measured quantity of reducing agent and the excess determined by titration with permanganate. Sometimes the analysis is finished by comparing the color of the permanganate produced by suitable oxidation with that corresponding to known quantities of permanganate. In this book four methods of analysis will be described.

Bismuthate Method[1]

$1000 \text{ ml } N\ KMnO_4 = 10.99 \text{ g Mn}$

This method originated with Schneider,[2] who used bismuth tetroxide as the oxidizing agent; but as the oxide is difficult to prepare free from chlorides, and traces of chloride interfere with the end point of the titration, it was abandoned by Reddrop and Ramage,[3] who proposed the use of sodium bismuthate, $NaBiO_3$. The product sold under this name is of more or less indefinite composition.

The determination is based on the fact that a manganous salt in the presence of nitric acid is oxidized to permanganic acid by sodium bismuthate.

$$2Mn^{++} + 5\mathbf{NaBiO_3} + 14H^+ \rightarrow 2MnO_4^- + 5Bi^{+++} + 5Na^+ + 7H_2O$$

The permanganic acid formed is very stable in a cold solution containing 20–40 per cent of nitric acid. In hot solutions the excess of bismuthate is rapidly decomposed and then the permanganic acid breaks down; as soon as a small amount of manganous salt is formed it reacts with the permanganic acid and manganese dioxide precipitates.

In the cold, however, the excess of the bismuth salt can be filtered off, an excess of ferrous sulfate added to the clear filtrate, and the excess determined by titrating with permanganate. The end point is sharp, and the method is extremely accurate except in the presence of cobalt.[4]

The following conditions are recommended by Blum. To the cold manganous solution containing 20–40 per cent nitric acid (free from nitrous acid) in a volume of 50–150 ml, add a slight excess of bismuthate (usually 0.5–1.0 g), agitate thoroughly for about ½ minute, wash down the sides of the flask with 3 per cent nitric acid,[1] filter through asbestos, wash with 100 ml of 3 per cent nitric acid, add a slight excess of ferrous sulfate, and titrate at once with permanganate.

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[1] A. A. Blair, *J. Am. Chem. Soc.*, **26**, 793. W. Blum, Reprint No. 186 from *Bull. Bur. Standards*, **8** (1912).

[2] *Ding. poly. J.*, **269**, 224.

[3] *Trans. Chem. Soc.*, **1895**, 268.

[4] G. E. F. Lundell, *J. Am. Chem. Soc.*, **45**, 2600 (1923).

Procedure. Dissolve 1 g of sample in 50 ml of 4 *N* nitric acid and boil the solution to expel oxides of nitrogen. Remove from the heat, add about 0.5 g of sodium bismuthate, and boil 2 to 3 minutes. If more than 0.1 per cent manganese is present, a precipitate of manganese dioxide usually appears or, if the manganese content is low, a pink color is produced. If neither a pink color nor a precipitate is produced, add more bismuthate and heat again. Clear the solution by adding a few drops of sulfurous acid, boil 2 to 3 minutes, and cool to 15°. Add 0.5 to 1 g more of bismuthate (enough to leave a *small* excess undissolved), agitate, and allow to stand for 1 minute. Then add 50 ml of 3 per cent nitric acid (3 ml of concentrated HNO_3 + 97 ml of water), and filter through asbestos. A suitable filter can be made by tamping down some glass wool in a funnel and pouring some asbestos fibers suspended in water upon it. If a Gooch crucible is used for filtering, take care that none of the filtrate comes in contact with the rubber that holds the crucible in the filter bottle. A glass filtering crucible can be used. Wash the excess bismuthate with 3 per cent nitric acid until the last runnings are colorless (50 to 100 ml of acid should be used). Add a measured volume of standard ferrous sulfate solution (usually a 25-ml pipetful is sufficient), and titrate the excess with permanganate.[2]

The ratio of permanganate to ferrous sulfate solution must be determined daily. Though not strictly necessary, the determination of this ratio by means of a blank affords a convenient means of testing the efficacy of the filter. The conditions found most satisfactory by Blum are: To 50 ml of nitric acid (25 per cent by volume), add a small amount of bismuthate; shake and allow to stand a few minutes, dilute with 50 ml of 3 per cent nitric acid; filter through the asbestos filter, and wash with 100 ml of 3 per cent nitric acid. To the filtrate, which should be perfectly clear, add a volume of ferrous sulfate approximately equal to that to be used in the subsequent determinations (25 or 50 ml), and titrate at once to the first visible pink. Even for the most accurate work, no end-point correction is required for this titration, provided only that the solutions are always titrated to the same color, and that about the same volumes are used in the standardization and analyses.

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[1] One ml of nitric acid, *d* 1.42, contains nearly 1 g of HNO_3. The solution of 3 ml concentrated nitric acid diluted to 100 ml is approximately a 3 per cent solution both by weight and by volume.

[2] H. F. V. Little, *Analyst*, **37**, 554 (1912), found that it was advisable to filter into a known volume of standardized ferrous solution when the manganese content was high.

The manganese content of the steel can be computed as follows:

Let s = weight of the sample.
A = volume of $KMnO_4$ which is equivalent to the $FeSO_4$ used.
n = volume of $KMnO_4$ used to titrate the excess $FeSO_4$.
N = the normality of the $KMnO_4$ solution.

$$\frac{(A - n)N \times 0.01099 \times 100}{s} = \text{per cent Mn}$$

It was originally assumed that the bismuthate method was not well suited for determining large quantities of manganese, but Cunningham and Coltman[1] have shown how the method can be applied to materials rich in manganese.

The following modification of the bismuthate method is useful for rapid work. It depends upon reducing the permanganate formed with a sodium arsenite solution. Sodium arsenite in dilute acid solution is oxidized to arsenate; but, under the conditions prevailing in this analysis, the reduction of the permanganate does not take place completely to the manganous condition. With a little practice, however, it is easy to note the point when all the permanganate has been acted upon, and this is taken as the end point although the solution has a greenish tint if much manganese is present.

Interfering Substances. Cobalt, cerium, and nitrous, hydrochloric, and hydrofluoric acids, large quantities of phosphoric acid, and, to a lesser degree, chromium and vanadium interfere with the bismuthate method. The carbonaceous residue obtained when cast iron is treated with nitric acid also interferes and must be filtered off. Interference of cobalt cannot be overcome as cobalt is oxidized to the cobaltic state and is subsequently reduced by the added ferrous sulfate. When cobalt is present, therefore, the persulfate method is to be preferred. Cerium is seldom present, but its interference can be overcome by titrating the permanganate, formed by the action of sodium bismuthate, with sodium arsenite, which does not reduce quadrivalent ceric ions. The error caused by chromium is not serious unless more than 1 per cent is present. Interference by large quantities of chromium can be overcome by removing the chromium in either of the following two ways: (*a*) Digest 1 g of sample with exactly 20 ml of 3.6 N H_2SO_4. Dilute the resulting solution to 100 ml with boiling water and add from a buret, while stirring, sufficient 8 per cent $NaHCO_3$ solution to give a permanent precipitate and 4 ml more. Boil 1 minute, filter off the $Cr(OH)_3$ and some $Fe(OH)_3$ formed by atmospheric oxidation, and wash 5 times with hot water. Pay no attention to a cloudy filtrate caused by the gradual oxidation of more of the ferrous iron. Use the filtrate for the manganese determination.

(*b*) Heat gently 1 g of sample in a 500-ml flask with a mixture of 1 part 2.5 N HCl and 4 parts of 72 per cent $HClO_4$. When the sample has dissolved, heat on the hot plate with gradually increasing temperature and finally fume 5 to 10 minutes until all the chromium is oxidized to CrO_3. Then, to volatilize the chromium as CrO_2Cl_2, add 1 to 4 g of NaCl in small portions until there are no more brown fumes of chromyl chloride. After the last addition of NaCl, boil the solution for 1 minute to remove HCl, add HNO_3, H_2SO_4, and H_3PO_4, and determine the manganese by the persulfate method (p. 260).

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[1] *Ind. Eng. Chem.*, **16**, 58–63 (1924). Cf. Little, *loc. cit.*

Persulfate Method[1]

In a hot solution of a manganous salt containing silver nitrate as catalyzer, ammonium persulfate causes the formation of permanganic acid.

$$2Mn^{++} + 5S_2O_8^{--} + (Ag^+) + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{--} + (Ag^+) + 16H^+$$

Without the silver salt, manganous acid, H_2MnO_3, is precipitated. In the routine analysis of steel it is customary to discharge the permanganate color by adding standard sodium arsenite. Under the conditions that usually prevail, the arsenic is completely oxidized to the quinquevalent condition; the manganese of the permanganate is not reduced to colorless manganous salt but to a solution which contains manganese partly trivalent and partly quinquevalent. The solution has greenish yellow tint at the end point when more than a few milligrams of manganese are present. The arsenite solution, therefore, must be standardized in exactly the same way it is used in the analysis against permanganate solution or by means of a Bureau of Standards steel. If, however, the titration is made with the following sodium arsenite and nitrite solution, the $HMnO_4$ is reduced completely to the bivalent state.[2] Dissolve 1.3 g of pure As_2O_3 in 25 ml of 4 *N* NaOH, dilute to 200 ml, make acid with dilute H_2SO_4, and then make neutral to litmus by adding $NaHCO_3$. Add 0.85 g of $NaNO_2$ and dilute to 1 l.

Dissolving Solution. Mix together 5 ml of 0.1 *N* $AgNO_3$, 40 ml of water, 2 ml of concentrated H_2SO_4, and 15 ml of concentrated HNO_3.

Titrating Solution. Dissolve exactly 0.337 g of pure As_2O_3 and about 1.1 g of Na_2CO_3 in about 60 ml of hot water. When the solids have dissolved completely, transfer to a liter measuring flask and make up to exactly 1 l. One milliliter = 0.1 mg Mn. Test the strength of the solution by taking a measured volume of 0.1 *N* $KMnO_4$ (2.00 ml is suitable), reducing it with a little H_2SO_3, and then proceeding exactly as in the analysis of steel, using the same quantities of reagents.

Procedure. Weigh out portions of exactly 0.100 g (within 1 mg) into 250-ml Erlenmeyer flasks, and heat each portion with 15 ml of the dissolving solution until all the steel has dissolved and the red nitrous fumes have been expelled. Remove from the hot plate; add 100 ml of hot water and 10 ml of 10 per cent $(NH_4)_2S_2O_8$ solution. Heat to boiling, and maintain this temperature for 30 seconds. Remove from the hot plate and cool under running water to about 15°. (If necessary use ice-water.) Titrate the cold solution until the permanganate color is discharged. Pay no attention to a return of the color on standing. (This can be prevented by adding to the *cold* solution just enough dilute NaCl to precipitate the Ag^+ as AgCl. In the absence of the Ag^+, Mn^{++} is not oxidized in the cold.)

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[1] Walters, *Proc. Eng. Soc. Western Pa.*, **17**, 257 (1901); *Chem. News*, **84**, 239, H. P. Smith, *Chem. News*, **90**, 237 (1904). Rubricus, *Chem. Ztg. Repert.*, **1905**, 247. F. Kunze, *Chem. Ztg.*, **29**, 1017 (1905). H. Marshall, *Z. anal. Chem.*, **43**, 418; 655 (1904).

[2] Sandell, Kolthoff, and Lingane, *Ind. Eng. Chem., Anal. Ed.*, **7**, 256 (1935).

The persulfate, in the presence of silver cations, slowly oxidizes the manganous ions to permanganate, but this reaction is so slow in the cold that there is no serious error if the titration takes place fairly quickly. If the cold solution is treated with just sufficient NaCl solution to precipitate the silver before the titration, the end point lasts much better; but if the solution is hot when the chloride is added, some permanganate is likely to be reduced. The above very rapid method has never been regarded as suitable for umpire analysis, but students usually obtain excellent results agreeing within 0.02 per cent, or less, of the correct values. If considerable manganese is present the solution is yellow or green at the end point, but the practiced eye can easily tell when all the permanganate color is gone.

Modified Williams Method

$$1000 \text{ ml of } N\ \text{KMnO}_4 = \frac{\text{Mn}}{2} = 27.47 \text{ g Mn}$$

The Williams method depends, in the first place, upon the precipitation of all the manganese as MnO_2 by boiling the manganous solution with concentrated nitric acid and potassium chlorate. The reaction has also been used in qualitative analysis.

$$\text{Mn(NO}_3)_2 + 2\text{KClO}_3 + \text{H}_2\text{O} \rightarrow \mathbf{MnO_2{\cdot}H_2O} + 2\text{KNO}_3 + 2\text{ClO}_2 \uparrow$$

The precipitate is dissolved in acid and a known quantity of reducing agent, and the excess of the latter is measured by titration with standard potassium permanganate solution. A standard solution of acid ferrous sulfate or ferrous ammonium sulfate is commonly used as the reducing agent, and since such a solution oxidizes slowly on standing in the air it is necessary to determine its strength at least once every day that it is being used.

Julian[1] used H_2O_2 as the reducing agent and did not bother to filter off the precipitate, but it is unquestionably better to do so because the presence of a little nitrous acid in the solution is likely to cause error in the final titration.

Procedure. Take 2 to 3 g of steel (weighed to the nearest centigram) in a 500-ml Erlenmeyer flask and dissolve it in 60 ml of 6 N HNO_3. When the steel has dissolved, evaporate the solution to sirupy consistency (about 10 ml); add 50 ml of concentrated nitric acid and 3 g of potassium chlorate crystals. Boil the solution on the hot plate for 15 minutes. Then remove the flask from the hot plate, as otherwise the ClO_2 which is liberated on adding chlorate may explode; add 15 ml more of concentrated nitric acid and another 3 g of potassium chlorate. Boil for another 15 minutes. Cool quickly by placing the flask in cold water and rotating the contents. Prepare an asbestos filter by pressing down a little glass wool in a funnel and pouring on it a little asbestos suspension such as is used for Gooch crucibles. Filter through the asbestos, and wash the MnO_2 precipitate with three 10-ml portions of cold water. Transfer the asbestos pad and precipitate back to the original flask. As solvent, prepare a mixture of 900 ml water, 43 ml of

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[1] *J. Am. Chem. Soc.*, **15**, 113 (1893); cf. *J. Anal. Chem.*, **2**, 249 (1888).

3 per cent hydrogen peroxide, 25 ml of phosphoric acid, *d* 1.70, and 25 ml of concentrated sulfuric acid; keep the solution in a glass-stoppered bottle. Of this well-mixed solution take out 25-ml portions by means of a pipet. Usually one portion of the solution is sufficient to dissolve the MnO_2 precipitate and leave an excess of H_2O_2. At the same time, take two separate portions of the solution for direct titration with permanganate. In every case, dilute with water to about 200 ml and titrate with standard potassium permanganate. In using the pipet make sure that it has been cleaned recently with cleaning solution so that it will drain well and that it has been rinsed out with three small portions of the solution which is to be measured. Make sure that the pipet is filled from the bottom up to the mark on the stem, and, after allowing the contents to drain out, touch the tip of the pipet to the side of the beaker just above the solution. When used in this way pipets are more accurate than the ordinary buret.

The reactions that take place with the hydrogen peroxide are these:

$$H_2O_2 + \mathbf{MnO_2} + 2H^+ \rightarrow Mn^{++} + 2H_2O + O_2 \uparrow$$
$$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{++} + 8H_2O + 5O_2 \uparrow$$

If, in the analysis of s grams of steel, 25 ml of H_2O_2 were used which were equivalent, as found by direct titration, to A ml of $KMnO_4$ and the excess H_2O_2 reacted with n ml of $KMnO_4$ which was N-normal, then

$$\frac{(A - n)N \times 0.02747}{s} \times 100 = \text{per cent Mn}$$

Volhard Method[1]

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{3\text{Mn}}{10} = 16.48 \text{ g Mn}$$

If an almost boiling, nearly neutral solution of manganese sulfate is slowly treated with a solution of potassium permanganate, each drop will cause the formation of manganous acid (H_2MnO_3). Under ideal conditions the reaction takes place as follows:

$$2MnO_4^- + 3Mn^{++} + 7H_2O \rightarrow 5\mathbf{H_2MnO_3} + 4H^+$$

According to this equation, $2KMnO_4$ (10 equivalents) react with $3Mn^{++}$ (cf. p. 110).

A. Guyard, who first determined manganese by this method, assumed that the oxidation took place according to the above equation.

In reality, however, instead of pure manganous acid being precipitated, different acid manganites of varying composition are formed; for example:

$$4KMnO_4 + 11MnSO_4 + 14H_2O = 4KHSO_4 + 7H_2SO_4 + 5\mathbf{Mn(HMnO_3)_2}$$

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[1] *Ann. Chem. Pharm.*, **198**, 318 (1879). Cf. W. Fischer, *Z. anal. Chem.*, **48**, 751, (1909); Cahin and Little, *Analyst*, **36**, 52 (1911). The method was really proposed first by Morawski and Stingl, *Chem. News*, **38**, 297 (1878).

Volhard has shown that if calcium, barium, or, better still, zinc salts, are present, manganites of these metals are precipitated. The precipitate, although varying in composition, then contains all *the manganese in the quadrivalent form.*

Weigh out, to three significant figures, three separate portions of 2 g of steel into 300-ml porcelain casseroles. Cover the dishes with watch glasses, and dissolve each sample by the gradual addition of 25 ml of 6 *N* nitric acid. When the sample has dissolved, raise the cover glass, evaporate to dryness, and ignite carefully to decompose nitrates. Cool and digest the residue with 20 ml of concentrated hydrochloric acid.

If a dark residue remains undissolved, evaporate the solution to dryness again, dehydrate silica by heating an hour at 125°, warm with 10 ml of concentrated hydrochloric acid, dilute, filter, and wash the residue thoroughly, first with a little hot 2 *N* hydrochloric acid, then with cold water, and finally with hot water. If there is no dark-colored residue containing graphite, this treatment is unnecessary. A carbonaceous residue is always more or less oxidizable and must be removed.

Evaporate the hydrochloric acid to dryness. Moisten the residue with 10 ml of 6 *N* hydrochloric acid, warm, and evaporate to a small volume but not to dryness. Transfer to a 500-ml measuring-flask, first filtering if there is much residue, and dilute with cold water to about 200 ml. Add 6 *N* sodium carbonate solution in small portions until the ferric chloride solution has a deep red color and then small quantities of a suspension of zinc oxide in water, shaking after each addition of oxide and continuing until a point is reached where the liquid suddenly coagulates forming a heavy precipitate of ferric hydroxide. Fill the flask with water up to the mark, mix thoroughly by pouring back and forth into a beaker several times, allow the precipitate to settle, and filter through an 18–20 cm filter. Reject the first 5 ml of filtrate and collect the next 250 ml in a measuring flask. Transfer the solution to a 500-ml flat-bottomed flask, add 5 ml of 6 *N* acetic acid, and titrate until the hot solution (80–90°) appears pink above the brown precipitate, best viewed in the neck of the flask against a light background. Add the $KMnO_4$ in ml portions to the first sample until the end point is overstepped. To the other samples, add nearly all the requisite $KMnO_4$ at once.

HOME PROBLEMS

19. If 40 ml of potassium tetroxalate solution reacts with 30 ml of 0.2 *N* sodium hydroxide solution and 60 ml of permanganate solution is required to oxidize 24 ml of the same tetroxalate solution, find the value of 1 ml of $KMnO_4$ in terms of Mn by the (*a*) Volhard method, (*b*) bismuthate method, (*c*) Williams method.

20. If a sample of steel weighing 0.9 g and containing 0.50 per cent Mn is used for analysis, how many milliliters of a solution of $KMnO_4$ (10 ml = 0.0630 g of $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$) will be equivalent to its manganese content by (*a*) the bismuthate method, (*b*) the Volhard method, (*c*) the Williams method?

21. What weight of steel should be taken for analysis so that the number of milliliters of $N/12$ $KMnO_4$ equivalent to the Mn in the steel is 8 times the per cent Mn in the steel if the analysis is made by the (*a*) Volhard method (one-half the solution is titrated), (*b*) bismuthate method, (*c*) Williams method?

22. From the following data compute the normality of a potassium permanganate solution, and show its value in terms of manganese by three methods of analysis:

$$\begin{aligned} 20 \text{ ml } KMnO_4 &= 45 \text{ ml } Na_2S_2O_3 \\ 20 \text{ ml } Na_2S_2O_3 &= 15 \text{ ml iodine} \\ 1 \text{ ml iodine} &= 0.00056 \text{ g sulfur } (H_2S + I_2 \rightarrow 2HI + S \end{aligned}$$

23. In the Volhard method for manganese, what weight of steel should be taken so that the milliliters of $N/10$ $KMnO_4$ shall equal 10 times the per cent Mn?

24. A sample of steel weighing 1.880 g contains 0.596 per cent manganese, and 9.49 ml of permanganate solution (1 ml = 0.007188 g sodium oxalate) is equivalent to the manganese. What method was used for the determination (Volhard, bismuthate, Williams)?

25. A sample of ferromanganese contains 80.25 per cent Mn. How many milliliters of $KMnO_4$ (1 ml = 0.00500 g Fe) are used for the titration of a sample weighing 0.300 g by the Volhard method? What would have been the apparent percentage if a minus error of 0.35 ml had been made in the buret reading of the permanganate solution?

26. In the analysis of a sample of steel weighing 1.5 g and containing 0.5 per cent Mn, the total Mn equivalent in terms of $KMnO_4$ solution is 3.96 ml. If 40 ml $KMnO_4$ = 0.3082 g $Na_2C_2O_4$ which method of analysis was used?

27. A sample of steel containing Mn is analyzed by the Williams method; the precipitate of MnO_2 is dissolved in 200 ml of oxalic acid containing 0.00200 g of $H_2C_2O_4 \cdot 2H_2O$ per milliliter and 20 ml of $N/10$ $KMnO_4$ is required for the excess. What volume of the $KMnO_4$ would have been used if the sample had been analyzed by the Volhard method (one-half the solution titrated) and starting with the same weight of steel?

CHAPTER XVII

CARBON IN IRON AND STEEL

Carbon occurs in iron and steel as carbide, as a solid solution of carbide in iron, as graphite, and as temper carbon. Iron carbide, Fe_3C, is often called cementite. The properties of iron and steel depend not only upon the chemical composition of the material but also upon the treatment which has been given to it. Thus a steel with a given percentage of carbon may be very hard if it has been cooled quickly from say 1000°, or it may be much softer if it has been annealed. By polishing a piece of metal and etching the surface, it is possible to estimate by microscopical examination the percentage of carbon present, the heat treatment which has been given to the specimen, and whether the material is homogeneous. In testing steel and other alloys the work of the chemist should go hand in hand with that of the metallographer as either is likely to be led astray without the other.

Here we shall assume that steel is a binary alloy of carbon and iron. This will carry us sufficiently into the field of metallography but it must be remembered that other elements, e. g., manganese, sulfur, silicon, chromium, nickel, tungsten, and vanadium, play important parts in modern steel-making. To understand the reasons for the various effects accomplished by heat treatment, it is necessary to know something concerning the laws of physical chemistry, especially the phase rule of Willard Gibbs. Here just a little of the theory will be touched upon.

The mass-action law, which has frequently been mentioned in this book, refers to what is called *homogeneous equilibria*. It governs, for example, the reaction between ions when everything is present in a state of aqueous solution. We say that this constitutes a single *phase*. Every homogeneous state which the components of a system can produce is called a *phase*; the phases, in other words, are the physical states in which the components can exist. A few illustrations will help here.

The compound H_2O can exist as solid, liquid, or gas, and each of these physical states represents a phase. A mixture of NaCl and H_2O can exist in four phases. If, at a low temperature, the two compounds exist side by side as solids which are distinguishable from one another (ice and salt), we say that two phases are present and the system is not homogeneous. As many solid phases can exist side by side as there are distinguishable solids. If we have a solution of NaCl in water, we have a single phase, and we say that we have a homogeneous system. If we add more water, more salt, or any other substance to the solution (and there is no precipitation), we still have but a single phase. If, on the other hand, we add ether to an aqueous solution, and can distinguish a line of demarcation between the two liquids, we have two phases. In any system there can be as many liquid phases as there are immiscible liquids or solutions. Gases, however, all mix with one another and constitute a single phase. What Gibbs did was to discover an important relation between the number of components, the number of phases, and the degrees of freedom of a system.

If we study the equilibrium conditions of water with respect to its existence as solid, liquid, or gas, we say that we are considering a *one-component* system. The number of components is the smallest number of independently variable constituents required to build up the system. In studying the reaction $CaCO_3 \rightleftharpoons CaO + CO_2$ we say that we have a *two-component system* because any desired state can be obtained from suitable quantities of CaO and CO_2 and it is not necessary to have all three present at the start. On the other hand, it is not a one-component system because it is not possible to get all sorts of mixtures of CaO and CO_2 from $CaCO_3$ alone.

In studying the equilibrium of a gas we determine pressure and temperature. If both temperature and pressure can be varied without changing the number of phases present, we have two *degrees of freedom*. In studying a solution of a definite substance in water we measure temperature and concentration, and we say that there exist two degrees of freedom if we can vary the temperature and concentration without causing the number of phases to change.

The Gibbs rule is

$$P + F = C + 2$$

when P is the number of phases, C is the number of components, and F the degrees of freedom in a state of equilibrium.

This is a very important generalization. Let us take a few examples. If we study the equilibrium conditions of a one-component system such as water, we find that we can express all possible conditions in terms of the two variants pressure and temperature. At 0.0076° and 4.57 mm of pressure, we can have existing together in perfect equilibrium the three phases, ice, water, and water vapor. Then applying the phase rule we have

$$3 \text{ phases} + 0 \text{ freedom} = 1 + 2$$

There is no freedom to the system when ice, water, and water vapor are existing together in a state of perfect equilibrium, and we have a state of *invariant* equilibrium. On the equilibrium diagram there is such a so-called *triple point* at 0.0076° and 457 mm pressure.

The system salt and water can be expressed in terms of concentration of the solution and temperature. At −22° and with about 23 per cent of dissolved sodium chloride, there can exist four phases in equilibrium side by side, and we have what is called a *quadruple point*. The four phases are water vapor, liquid solution, solid ice, and solid salt. If either the concentration of the solution or the temperature is changed, one phase will disappear. For a two-component system, $P + F = 2 + 2$; and when all four phases are present together, there is no freedom and the system is in a state of invariant equilibrium.

The alloys of iron and carbon can be studied on this basis. In reality the alloys contain more than two components, Fe and C, but it is simplest to study them on this basis and then find the effect that other constituents exert. Figure 40 is an equilibrium diagram of iron and carbon. Temperatures are plotted as ordinates and concentrations of carbon as abscissas.

In applying the phase rule to this diagram, it is assumed that the vapor phase is always present although to an inappreciable extent. Neglecting this phase, the rule becomes $P + F = C + 1$, which means that the system has no freedom, or is *invariant*, when three solids or two solids and a liquid exist together. If the temperature is changed, one phase disappears. The diagram shows two such points, *E* and *P*. At *E* (4.3 per cent C and 1100°) the melt can exist in equilibrium with two solids, called *austenite* and *cementite*. The intimate mixture of these two phases which exists in equilibrium with the molten metal at *E* is called a *eutectic*. Cementite is the metallographic name given to Fe_3C; austenite is the name given to a solid solution (mixed crystals) of Fe_3C in Fe. According to its appearance under the microscope, the solid solution of Fe_3C in Fe is given different names. Austenite may be assumed to repre-

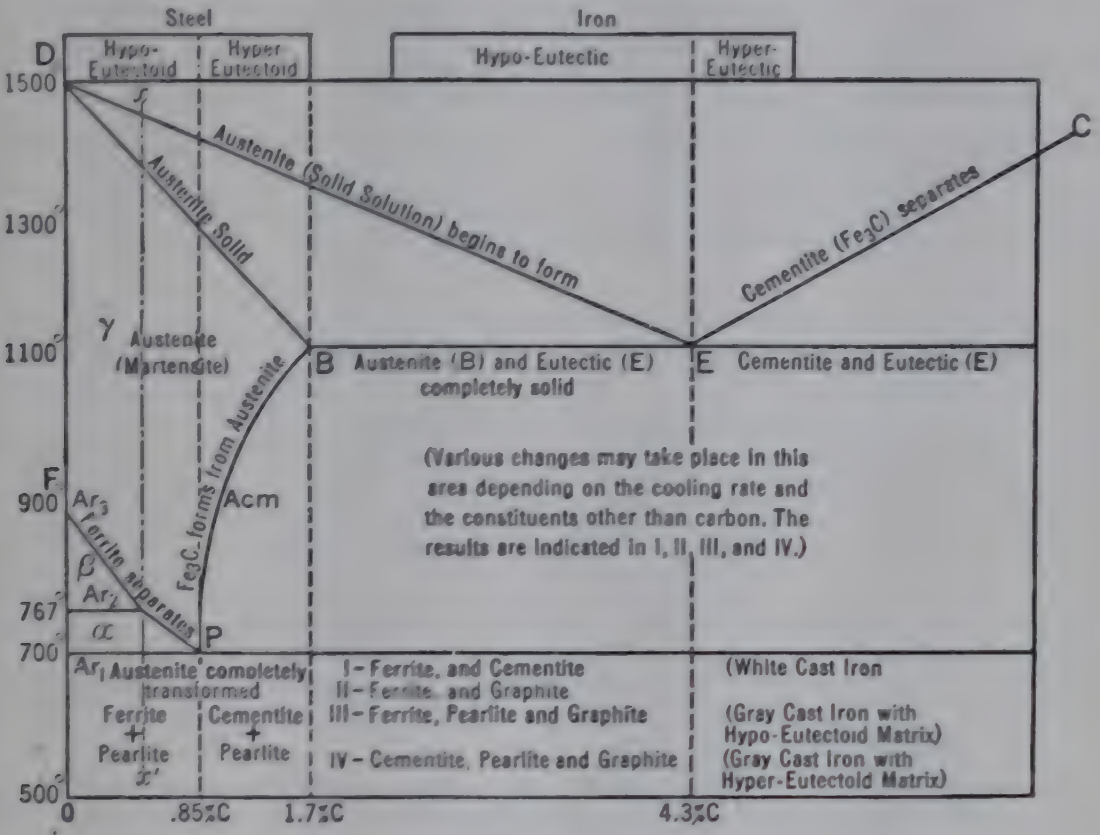
Steel
Iron
Hypo-Eutectoid
Hyper Eutectoid
Hypo-Eutectic
Hyper-Eutectic
D
1500
1300
1100
F
900
767
700
500
0
.85%C
1.7%C
4.3%C
C
S
Austenite (Solid Solution) begins to form
Austenite Solid
Cementite (Fe_3C) separates
γ Austenite (Martensite)
B
Austenite (B) and Eutectic (E) completely solid
E
Cementite and Eutectic (E)
Fe3C forms from Austenite
Acm
(Various changes may take place in this area depending on the cooling rate and the constituents other than carbon. The results are indicated in I, II, III, and IV.)
Ar3
Ferrite separates
β
Ar2
α
P
Ar1 Austenite completely transformed
Ferrite + Pearlite
x'
Cementite + Pearlite
I – Ferrite, and Cementite
II – Ferrite, and Graphite
III – Ferrite, Pearlite and Graphite
IV – Cementite, Pearlite and Graphite
(White Cast Iron
(Gray Cast Iron with Hypo-Eutectoid Matrix)
(Gray Cast Iron with Hyper-Eutectoid Matrix)

FIG. 40.

sent the solid solution in the state in which it exists at high temperatures. On cooling it tends to break down into iron and cementite, and the point *P* on the diagram is where an intimate mixture of Fe and Fe_3C, called *pearlite*, is in equilibrium with the solid solution of Fe_3C in Fe. As the austenite breaks down into Fe and Fe_3C, it passes through the stages called martensite, troostite, and sorbite. The transition to martensite takes place so readily that austenite is seldom found in commercial steels. Troostite and sorbite have been called colloidal solutions of Fe_3C in Fe.

The point *P* on the diagram has been called the *eutectoid* point, but the name pearlite is commonly given to the Fe-C alloy of this composition because, when the annealed sample is polished and etched slightly, the "eutectoid" shows under the microscope a luster similar to that of mother-of-pearl.

If a sample of Fe-C alloy with, say, 1 per cent of carbon is cooled slowly from the molten state and the temperature is plotted against the time, the rate of cooling will lag a little, showing an evolution of heat due to the separation of a solid, when the line *DE* is reached. The solid that separates out is austenite of the composition corresponding to that temperature, as is shown by drawing a horizontal line across to the line *DB*. As the temperature falls, the freezing point of the alloy follows the line *DE* and the carbon content of the solid solution follows the line *DB*. Since less than 1.7 per cent carbon is present, the only product on solidification will be austenite. If more than 1.7 per cent of carbon is present some eutectic will be formed at 1100°, the amount increasing as the C content approaches 4.3 per cent; an alloy of 4.3 per cent C and 95.6 per cent Fe will solidify entirely at 1100° and show a melting point as sharp as if it were a pure compound.

The region above the lines *DEC* in the diagram represents molten metal and a field of bivariant equilibrium. The region *DBPF* represents austenite, or solid solution, and another field of bivariant equilibrium. The lines *FPB* shows where the solid solution should break down, and on these lines there is univariant equilibrium except at the point *P*. *FP* shows where pure Fe separates out until, at 700°, pearlite is deposited. The line *BP* is where Fe_3C separates out.

On the diagram three critical points are shown at Ar_1, Ar_2, and Ar_3. These are said to mark three allotropic forms of Fe: α-Fe is stable below 767°, β-Fe between 767° and 900°, and γ-Fe above 900°. Carbon is soluble only in γ-Fe, so that we may say that the field *DBPF* represents the region where a solution of C (or of Fe_3C) in γ-Fe exists.

All the transformation points in the equilibrium diagram are found a few degrees higher when they are approached with rising temperature, and that is why a distinction is made between Ar_1, Ar_2, Ar_3 and Ac_1, Ac_2, Ac_3 the letters *r* and *c* referring respectively to the French words *refroidissement* and *chauffage*.

A sample of steel cooled slowly so that all the transformations are allowed to take place should contain ferrite + pearlite if it contains less than 0.85 per cent C and cementite + pearlite if it contains more than 0.85 per cent C. If the steel is cooled rapidly (quenched) from a temperature above the *FPB* line, the condition existing at the temperature from which the quenching took place is retained. The steel is in a strained state and is very much harder than if it had been allowed to cool slowly. If the steel is heated the transformation into the stable condition begins to take place before the *FPB* line is reached.

On slow cooling of *irons* the metal should consist of austenite + eutectic or cementite + eutectic, but the Fe_3C is not very stable and it may break down into Fe and C. The presence of silicon tends to hasten this change, and when the C has deposited as graphite we have a *gray cast iron.* Sulfur tends to prevent this breaking down of the Fe_3C, and when no graphite is formed we have a *white cast iron* which is very hard and also brittle.

This is not the place to go deeply into the metallography of iron and steel, but it seems desirable that every analyst should know that the condition of the carbon is just as important as the quantity of carbon in determining the properties of steel and that the heat treatment given the steel may change its properties entirely.

The chemist distinguishes between total carbon, combined carbon, and graphite. In steel, usually no uncombined carbon is present; and although attempts have been made to distinguish between combined carbon that is present as cementite, Fe_3C, and that present in solid solution (martensite, austenite, etc.), which has been called "hardening carbon," the total carbon is the only determination that the chemist is usually asked to make on steel. In the analysis of irons, usually the total carbon and the graphite are determined and the combined carbon is found by difference.

In the chemical analysis of iron and steel the total carbon is usually obtained by combustion. In this country, this is usually done in the dry way with an electric furnace. In some parts of Europe a wet combustion, or oxidation by a mixture of chromic and sulfuric acids, is preferred. For a long time it was considered desirable to remove the iron by volatilization in a stream of chlorine (Wöhler) or by treating the metal with a solution of double chloride of copper and potassium (Berzelius-Richter), but at a temperature of 1100° it is possible to get complete oxidation of the sample without removing the iron, and the procedure is thus shortened.

The combined carbon is sometimes determined quickly by matching the color of the solution obtained by dissolving the steel in nitric acid, but the color is not strictly proportional to the carbon content and a hardened steel gives a different color from that given by an annealed steel with the same carbon content. If speed is required, it is possible to determine carbon by combustion in less than 10 minutes, so that there is no longer any excuse for carrying out the colorimetric determination except in small steel works with limited laboratory equipment.

The carbon content can be estimated quite closely by means of a microscopic examination of the etched, polished surface of a sample of steel. Spark testing has also been used. In the old days the steel was "struck" with flint, but later special grinding wheels were used which, in conjunction with carefully prepared standards, made it possible to estimate the carbon within a few hundredths of 1 per cent. The electrical-resistance or Enlund method is based upon the fact that elements dissolved in iron increase the specific electrical resistance by an amount inversely proportional to their atomic weights, and carbon can be held in solid solution or thrown out at will in the case of steels by cooling slowly or by quenching. The difference between the specific electrical resistance of a properly prepared and quenched sample and that of the same or a similar specimen which has been annealed or normalized gives a factor from which the percentage of carbon can be calculated. Finally the magnetic method depends upon the fact that the incremental permeability of steel as measured by the deflection of a ballistic galvanometer is proportional to the carbon content. Other alloying elements have a similar effect, so that this method of testing, which can be carried out with an instrument called the *carbometer*, is restricted to the preliminary testing of plain-carbon steels made by the open-hearth or by the Bessemer process.

In classifying steels according to the carbon content, it is quite common to call each 0.01 per cent of carbon a *point*. Thus a 10-point carbon steel is one containing 0.10 per cent carbon.

Determination of Total Carbon by Direct Combustion in Oxygen

Apparatus. A suitable arrangement is shown in Fig. 41 together with some parts that can usually be omitted. The entire set-up is called a *combustion train*, and the *front end* is on the right where the excess oxygen leaves the apparatus. Sometimes this is called the *exit end*. Beginning at the back end, *A* represents a cylinder of oxygen which can be purchased filled with oxygen of about 95 per cent purity and free from CO, CO_2, or any other acidic gas or carbon-bearing material. If oxygen of this purity cannot be obtained, special provision must be made for purifying it in the train. *B* represents a reducing valve whereby oxygen can be forced at an easily regulated speed through the apparatus. The reducing valve must be capable of stepping down the pressure of the gas so that it can be made to leave the valve at a pressure of not more than 2 pounds per square inch and permit a steady flow throughout the train.

C represents a purifying train. With oxygen of the above-mentioned purity there is no need of this, but it is customary to insert here a CO_2 absorber, such as a soda-lime or an Ascarite tube. If the oxygen is not pure it must be passed through a tube loosely packed with ironized asbestos which is heated to about 600°. This causes combustion of CO or any other carbon compound in the gas, and the CO_2 formed is absorbed in a tube containing soda-lime or Ascarite. To prepare the ironized asbestos, saturate some well-shredded asbestos with 10 per cent ferrous sulfate solution, which is slightly acid with sulfuric acid, dry, and finally ignite at 1000° for 6 to 8 hours.

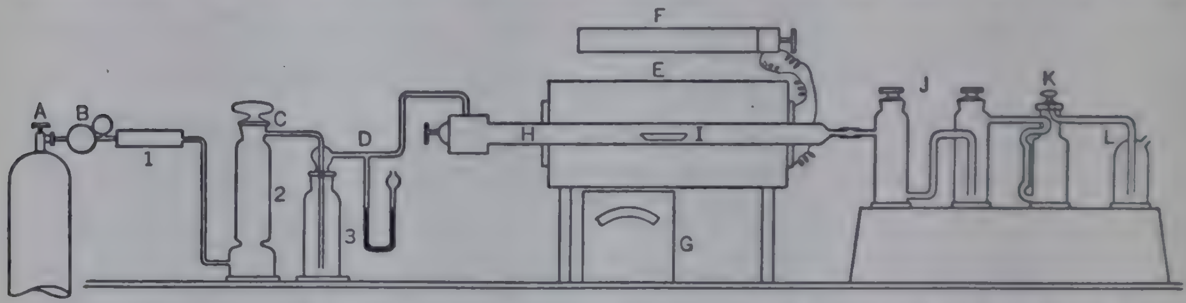

FIG. 41. Diagram of combustion train for the determination of carbon in steel.[1]

In Fig. 41, 1 represents the preheater, 2 is an absorption tube containing soda-lime or Ascarite, and 3 is a drying tube containing an efficient dehydrating agent such as fused calcium chloride, Drierite, Anhydrone, phosphorus pentoxide, or Dehydrite. It is best to use here the same absorbents for CO_2 and H_2O that are used at the other end of the train. It is important to have these gases removed with the same efficiency at both places.

D represents a mercury trap or manometer. It serves to give a rough idea of the prevailing gas pressure and to prevent the backflow of gas. It is not at all necessary to have this manometer, but it is convenient to have some means of knowing that the pressure of oxygen is being maintained. This is sometimes shown by inserting a liquid absorbent for CO_2 or a tube containing concentrated sulfuric acid at the front end of the apparatus, but the use of liquids is not to be encouraged except at the extreme front end of the train (*L* in Fig. 41).

The electric furnace is shown at *E*. A furnace capable of giving temperatures between 1000° and 1100° is satisfactory. It has been claimed that temperatures above 1150° are likely to cause reduction of some CO_2 before it can be taken away from around the boat, but experiments with temperatures as high as 1400° with a combustion tube at least 1.125 in. in diameter and a sufficiently rapid stream of oxygen have failed to substantiate this claim. The furnace should operate on either 110 or 220 volts. A new furnace should be heated slowly to the desired temperature or the refractory may crack and crumble away from the outer insulation. Low-temperature furnaces for operating below 1100° are generally wire wound and are best operated at low voltages with an alternating current and transformer.

It is possible to make the furnace in the laboratory. To do this wrap the porcelain combustion tube in a thin sheet of asbestos and wind around it about 110 turns

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[1] *Sampling and Analysis of Carbon and Alloy Steels*, Methods of the Chemists of United States Steel Corporation.

(40 ft.) of No. 20 B and S gauge nichrome wire in a space of about 7.5 in. along the tube. Then cover the wire thoroughly with *Alundum cement*, dry, and encase it in an insulating shell. This shell should be about 6 in. in diameter and 9 in. long, packed with asbestos pipe lagging. Close the ends with disks of Transite that carry the wire terminals. Laboratories where many combustions are made sometimes require multiple furnaces carrying as many as five combustion tubes.

At *F* in Fig. 41 is a rheostat whereby the temperature can be kept within the operating limits. With proper attachments it is possible to make the temperature control automatic, and this is advisable when many combustions are to be made.

To operate a furnace without automatic temperature control a pyrometer is necessary as temperatures above 950° cannot be judged closely with the eye. The hot junction of the thermocouple should be located within the heating chamber as near the combustion tube as possible. With temperatures of about 1000° the pyrometer is not necessary except for checking the eye readings. An optical pyrometer focused on the end of the boat can be used. Gold melts at 1063°, and a correct operating temperature is one at which gold melts.

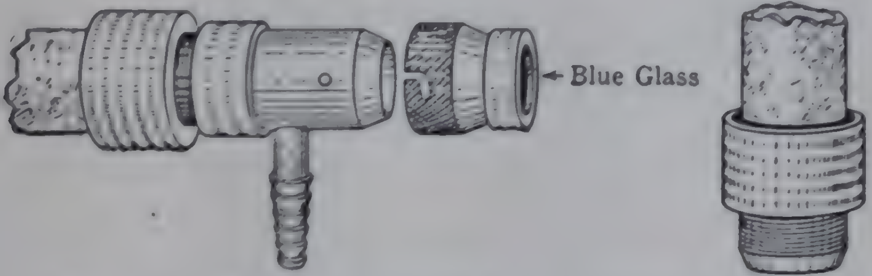

Fig. 42.— Breech connector for combustion tubes.

The combustion takes place preferably in a combustion tube of unglazed vitrified clay or porcelain though some brands of fused quartz can be used up to 1200°. The combustion tube should be about 28 in. long and have an internal diameter of about 1.2 in. The exit end of the tube is preferably reduced in diameter to permit connection with rubber tubing. Such a tube is shown at *H* in Fig. 41. The front end of the tube remains cooler if the reduction in size is made in two steps. The inlet end of the combustion tube is preferably provided with a breech connector which can be attached to the combustion tube by *plaster of paris* mixed with 2 per cent acetic acid. Sometimes a ground-glass stopper fits this end of the tube. If a rubber stopper is used, it should be provided with a suitable shield against the heat or it should be water-cooled. Figure 42[1] shows a breech connector which is made of brass, has a blue-glass window, and connects to the body by a bayonet joint which tightens as it is turned clockwise.

If provision is made for the absorption of oxides of sulfur in front of the combustion tube, no packing is necessary. When combustions take place continuously at 1000–1050°, the exit end of the tube can be packed with ironized asbestos to remove oxides of sulfur and selenium. After about 150 combustions, the tube should be drawn into the furnace and heated to expel the oxides of sulfur.

Boats and Lining. Boats made of porcelain, refractory clays, sheet nickel, or Alundum are satisfactory. The lining or bedding material for the sample is alkali-free Alundum of 60–90 mesh, high-grade chrome ore, or Zirkite. The chrome ore should be crushed, sized, washed with dilute HCl, dried, and ignited. Zirkite is the trade name for a preparation containing natural zirconium minerals. The blank and its lining should give a blank of not over 0.0005 g when heated to 1500° in oxygen as in a combustion. To prevent injury to the combustion tube from spattering it is well to use a cover for the boat which has an opening at both ends, rests entirely upon the lining, and is high enough to permit an unrestricted supply of oxygen to reach the sample. The boat is shown at *I* in Fig. 41. The approximate outside dimensions are: width, 0.75 in.; depth, 0.5 in.; and length, 4–6 in.; with walls as thin as practical.

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[1] From H. Lundell, Hoffman, and Bright. *Chemical Analysis of Iron and Steel.*

In Fig. 41, *J* represents a purifying train for the removal of dust, SO_2, etc. Various combinations have been recommended, such as: (1) glass wool, lead dioxide, or zinc shot and dehydrite; (2) precipitated neutral manganese dioxide followed by Dehydrite, Anhydrone, or phosphorus pentoxide; (3) a 50 per cent solution of chromium trioxide or a 5 per cent solution of potassium permanganate followed by concentrated sulfuric acid and Anhydrone; (4) a tube containing chromium trioxide in granular form followed by a saturated solution of chromium trioxide in concentrated sulfuric acid and a tube of P_2O_5 or the same desiccant used in the preceding tube. Objections have been raised against lead dioxide, zinc shot, or any liquid in the train, and the chemists of the United States Steel Corporation prefer neutral manganese dioxide which is prepared as follows:

Dissolve 50 g of $MnSO_4 \cdot 5H_2O$ in 625 ml of water, make the solution ammoniacal, and add 1 l of water containing 56 g of freshly dissolved $(NH_4)_2S_2O_8$. Boil 10 minutes with the addition of sufficient ammonia from time to time to keep the liquid ammoniacal. Allow the precipitate to settle, but, if the supernatant liquid remains cloudy, add 15–25 ml more of the persulfate solution and boil another 10 minutes. Allow the precipitate of MnO_2 to settle, carefully siphon off the supernatant solution, and wash by decantation with four 250-ml portions of hot water. Finally wash twice in the same way with dilute sulfuric acid and then filter through a thin felt of asbestos on a 2-in. filtering disk which is placed in a large funnel. Wash with hot water until free from sulfate, dry at 105° in a clean porcelain dish, grind to pass a 20-mesh sieve, and again dry thoroughly at 105°.

To prepare the absorption tube for sulfur-containing gases, place some ironized asbestos in the bottom of a Midvale tube (see p. 215) and fill within about an inch of the top with an even distribution of coarse and fine MnO_2; then pack with a plug of glass wool at the top and close with a one-holed rubber stopper carrying capillary tubing. This tube may require conditioning to prevent absorption of CO_2. Place it in the combustion train just behind the drying tower, and run two blank determinations with a high-carbon steel sample. If the carbon result is low, repeat with a high-sulfur steel. One filling should last for several hundred combustions.

K in Fig. 41 represents the weighed tube in which the carbon dioxide is absorbed. A Midvale tube such as is shown in Fig. 31 on p. 215 is suitable. It is filled with glass wool at the top and bottom, Ascarite or soda-lime, and the same desiccant as used in *J*. Fill a newly packed tube with oxygen, weigh, and run a blank with a steel containing a known quantity of carbon. This tube should have as counterpoise a similar tube which is kept near it at all times.

L in Fig. 41 is a gas-flow indicator. Usually concentrated sulfuric acid is used, and the rate at which bubbles of gas pass through it shows whether there is a sufficient supply of oxygen.

Before starting an analysis, observe the following precautions:

1. First test to see if there are any leaks. Close the stopcock at *K* in Fig. 41, make sure that the valve at *A* on the oxygen tank is open

sufficiently, and then carefully turn the needle valve at *B* to permit oxygen gas to enter the train. If the apparatus is tight, it can be told by watching the manometer tube at *D*. If this is not used, leave the stopcock at *K* open and close the exit at *L* before opening the valve at *B*.

2. Allow oxygen to pass through the furnace heated to 1000° for at least 15 minutes, introduce the boat with its lining of Alundum, attach the weighed absorption bulb *K*, and proceed exactly as in a determination (see below). Weigh the tube again against its counterpoise and, if necessary, continue this heating as in a determination, until the blank is within 0.0005 g. Sometimes it is well to carry out a determination with a Bureau of Standards sample of steel.

Procedure. After the train has been tested and the furnace is at 1000° weigh the absorption tube to the nearest 0.0001 g against its counterpoise. The absorption bulb can be of the Midvale, Nesbitt, Fleming, Newburgh, Vanier, Muehlberg, Richards, or Miller type; all are satisfactory. In Chapter XII of Part I, the Midvale tube was recommended, and it was assumed there that the Ascarite was its own drier. Numerous experiments have shown that this is true, but in determining small quantities of carbon it is well to place a little Anhydrone or phosphorus pentoxide at the top of the bulb where the gas leaves the bulb. The same desiccant should be used as was placed in *J* of Fig. 41. A newly packed bulb should be filled with oxygen to replace the air and allowed to stand in the balance case at least 5 minutes before weighing. The bulb and its filling should not weigh over 100 g, and it is best weighed against another tube of the same kind as counterpoise. A freshly filled bulb can be used for many determinations but it should be refilled when half the Ascarite contents of the tube have become discolored and nearly white.

Make a V-shaped groove or furrow in the bedding or lining of the boat, which has already been tested by the blank run, and weigh out 1.364 g of ordinary steel or 2.727 g if the carbon content is low. These are factor weights; the value of the fraction $\frac{\text{atomic weight C}}{\text{mol. weight CO}_2}$ is 0.2727, and if the sample of steel weighs 1.364 g the percentage of carbon is found by multiplying the weight of CO_2 in grams by 20. Time is saved in a busy laboratory and there is less chance for making an error in calculation if a factor weight or some multiple of it is used.

Before high temperatures were available, it was customary to add an accelerator to the charge to ensure complete combustion. With a furnace capable of a working temperature of 1200°, an accelerator is rarely necessary. Tin is the best accelerator for steels, and when 0.5 g of pure 20–40 mesh tin is added to the top of the charge in the boat, most alloy steels can be burned satisfactorily at 1050°. With very highly alloyed metals such as ferrochrome, tin alone is inadequate and it is necessary to add some pure, hydrogen-reduced iron or 2.727 g of a standard sample of commercially pure iron with known carbon content.

Spread out the sample in the groove, and over this place a suitable cover. Insert the boat into the back end of the combustion tube and, with a clean rod or piece of stainless-steel wire, push the boat forward about 3 or 4 in. and let it warm up there for about a minute before pushing it into the hottest zone of the tube. This procedure is desirable with tubes that are sensitive to thermal shock such as results when a cold boat is placed at once into the hottest part. As soon as the boat has been pushed to the position shown at *I* in Fig. 41, close the tube and turn on the oxygen slowly until the flow is 300 to 500 ml per minute; the larger flow is used in routine work where many determinations have to be made. The burning of the steel will be shown by a diminished flow of gas at the front end of the train. The combustion should be completed in 4 or 5 minutes. Reduce the flow of oxygen to about 150 ml, and allow 7–10 minutes to sweep out the products of combustion from the furnace. Then close the oxygen valve, disconnect the weighed Ascarite bulb, and let it stand in the balance case at least 2 minutes before weighing. The absorption bulb and its counterpoise, before being placed on the balance pans, should be momentarily opened to the air to bring the pressure inside to that of the air.

Meanwhile withdraw the boat from the furnace by means of a long, heavy wire bent at the end, examine the contents for complete combustion, and place in a desiccator to cool for the next charge. If the fusion appears incomplete, repeat the determination with a higher temperature or with more accelerator. It should be remembered, however, that it is possible to burn out all carbon from the chips without actually fusing them, although this may require 30 minutes or more. Results obtained by pulverizing the residue and reburning are usually less satisfactory than those obtained by starting with a new sample.

Volumetric Method

The apparatus and procedure are the same except that a Meyer tube with 8 to 10 bulbs containing excess $Ba(OH)_2$ is used in place of the weighed Ascarite bulb, the flow of oxygen should be only about 150 ml per minute, and about 25 minutes should be allowed for burning the carbon and sweeping out the furnace. After the combustion, the excess $Ba(OH)_2$ is titrated with standardized HCl to a phenolphthalein end point. The precipitated $BaCO_3$ does not dissolve until the *p*H is considerably lower than that at which phenolphthalein is decolorized.

Standard Hydrochloric Acid. Mix 8 ml of concentrated HCl with 1 l of water and standardize as described on p. 70.

Standard Barium Hydroxide. Dissolve 20 g of $Ba(OH)_2 \cdot 8H_2O$ in 1 l of freshly boiled and cooled water. Filter through a large and rapid filter paper in a 5-in. funnel, and keep in a bottle which is provided with a guard tube filled with Ascarite or soda-lime and with a siphon attached to an overflow 80-ml pipet (cf. Fig. 6, p. 74). To standardize this solution, take exactly 80 ml of it, add 25 ml of water and 2 or 3 drops of phenolphthalein indicator solution, and titrate with the standardized HCl until the phenolphthalein is decolorized. Add the acid slowly toward the last so as not to overstep the end point.

Procedure. Weigh out the sample exactly as in the previous method and have it ready to be inserted into the combustion tube. Transfer exactly 80 ml of the standardized $Ba(OH)_2$ solution to the 500-ml heavy Erlenmeyer flask shown in Fig. 43,[1] avoiding contact with the air as much as possible. Immediately insert the rubber stopper which carries the Meyer bulb tube and an inlet tube for the gases from the furnace. Connect the inlet tube to the front end of the combustion train, and omit

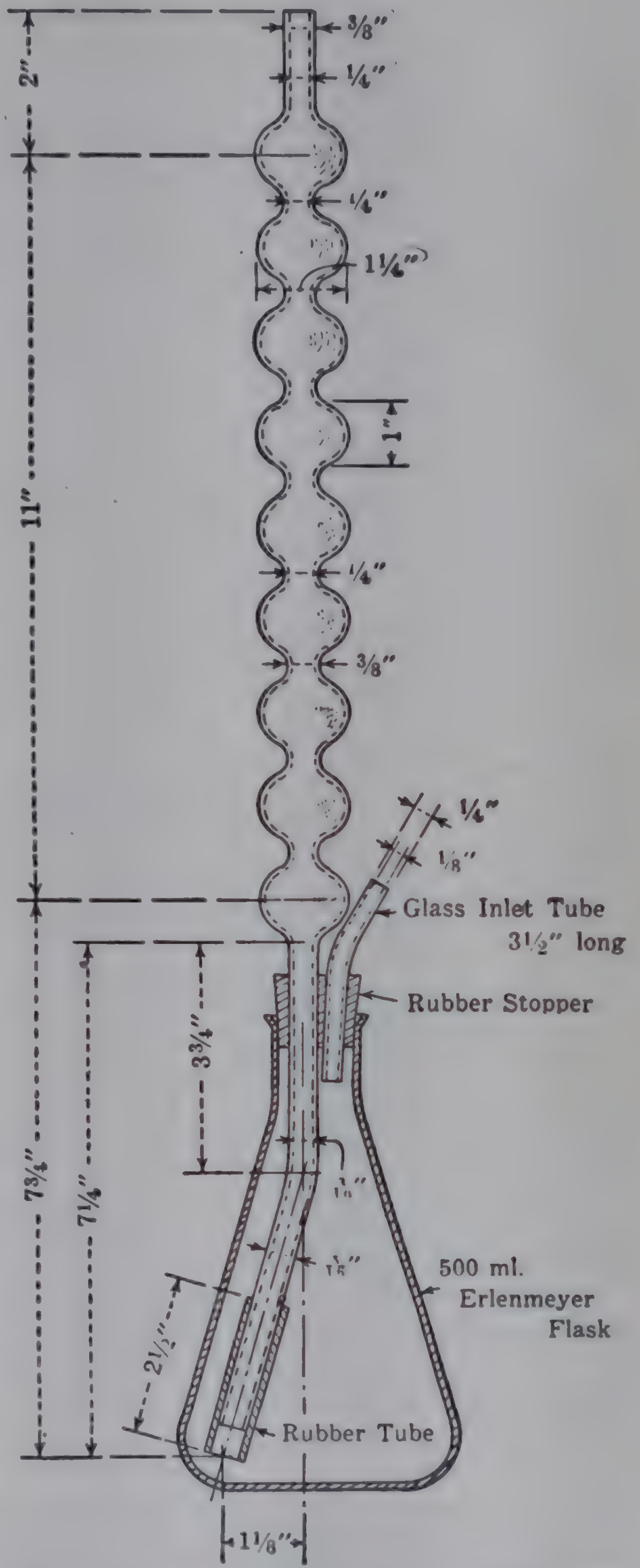

FIG. 43.— Flask and bulbs for absorbing CO_2 in $Ba(OH)_2$. The flask and the tube are supported at an angle of 45° to the table, during the combustion of the steel.

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[1] From Lundell, Hoffman, and Bright, *Chemical Analysis of Iron and Steel*. The directions are those of the chemists of the United States Steel Corporation.

the gas-flow indicator shown at *L* in Fig. 41. Support the flask and the Meyer tube in an inclined position so that the liquid in the flask will be forced into the bulb tube by the gas from the furnace. Insert the boat into the combustion tube, turn on the oxygen gradually, and adjust it during the combustion so that an excess of oxygen gas is always present and gas is constantly bubbling slowly through the absorption gas. Note the appearance of the $Ba(OH)_2$ solution, which will become distinctly turbid in about 5 minutes, showing that oxidation of the sample has begun. If necessary, increase the flow of gas while the sample is burning and then reduce it to the normal rate of about 150 ml per minute. Continue the flow of oxygen about 20 minutes longer, turn off the oxygen, and disconnect the absorption flask.

Hold the flask so that the bulb tube is in a vertical position; as the solution flows into the flask, rinse the bulbs with a stream of cold water which is free from CO_2, and gradually raise the stopper. Finally, when the inside of the bulb tube has been washed with about 25 ml of water and the bulb tube has been raised above the liquid, wash the outside of the tube where it came in contact with the solution. Add 3 drops of phenolphthalein solution and titrate slowly with the standard HCl, agitating the contents enough to ensure complete mixing but avoiding shaking with air. Take the disappearance of color as the end point. Deduct the volume required from that used in the standardization of the $Ba(OH)_2$, and the difference gives the milliliters of HCl equivalent to the carbon of the sample. One milliliter of 0.1 *N* HCl = 0.0006000 g C. From the standardization value of the acid the exact value in terms of C can be easily calculated; the solution is approximately 0.1 *N*.

It is common practice among steel chemists to standardize the HCl solution against a standard steel. This is not to be recommended because, when a sample of steel is certified to contain 0.419 per cent carbon, the values actually obtained by different analysts have sometimes ranged from 0.401 to 0.440, which corresponds to a deviation of about 10 per cent of the actual carbon content. Such an error would be inexcusable in a standardization of HCl against pure Na_2CO_3. A certified steel should be used to check a method of analysis but never for standardizing solutions to be used in an accurate analysis that takes place as represented by chemical equations.

Determination of Graphite

Dissolve 1 g of cast iron in 50 ml of 6 *N* nitric acid in a 300-ml beaker and heat gently until there is no further evolution of gas. By this means the carbide carbon is dissolved while the graphite is not attacked. Filter the solution through an ignited asbestos filter; wash the residue with hot water, then with a hot solution of potassium hydroxide (*d* 1.1), followed by hot water, dilute hydrochloric acid, and finally with hot water again until free from chloride. After drying at 110°, transfer the asbestos and graphite to a combustion tube and burn the carbon in a current of pure oxygen as described on p. 273.

Instead of weighing the CO_2 formed by combustion or measuring the volume of $Ba(OH)_2$ required to react with the CO_2, numerous other procedures have been proposed. Sometimes the $BaCO_3$ is filtered out of contact with air, the filtered precipitate is dissolved in a measured volume of standard acid, and the excess acid is back-titrated with base to a methyl orange end point. The determination has also been based upon the electrical resistance of 200 ml of $Ba(OH)_2$ solution before and after the absorption of CO_2, and sometimes the volume of the CO_2 gas has been measured. In laboratories where an electric furnace is not available, wet combustion with CrO_3, concentrated sulfuric acid, and a copper salt as catalyst has proved successful. One of the late developments has been the simultaneous determination of the CO_2 and the SO_2 formed from the sulfur in the steel. Several procedures for doing this have been recommended.

HOME PROBLEMS

28. If a 3-g sample of iron containing 1.15 per cent carbon is analyzed by direct combustion, what will be the gain in weight of the Ascarite tube? If the CO_2 formed is passed through 100 ml of $N/12$ $Ba(OH)_2$, how many milliters of $N/10$ HCl would be required to dissolve the filtered $BaCO_3$ precipitate?

29. What is the percentage of carbon in a 5-g sample of steel if on combustion the Ascarite tube gains 0.1601 g in weight? Using the same weight of sample and passing the gas into $Ba(OH)_2$ solution, what must be the normality of an HCl solution so that the number of milliliters required to titrate the $BaCO_3$ precipitate will be 25 times as large as the percentage of carbon?

30. A sample of steel weighing 4 g is to be analyzed for carbon by passing the gaseous combustion products through 50 ml of standard $Ba(OH)_2$ solution, filtering, and titrating the filtrate with standard HCl solution. It is desired to prepare the two solutions of such normality that by subtracting the buret reading from 100 the resulting value will be 30 times the percentage of carbon. What must be the two normalities?

31. What weight of steel should be taken for analysis by the gas-volumetric method such that each milliliter of CO_2 (S.T.P.) will represent 0.1 per cent of C in the sample?

32. Find the percentage of carbon in a sample of steel if the CO_2 from 2 g of sample is absorbed in 80 ml of $Ba(OH)_2$ solution containing exactly 20.00 g $Ba(OH)_2 \cdot 8H_2O$ per liter and after the absorption 24.0 ml of 0.25 N HCl is used in titrating the excess absorbent.

33. With samples of steel weighing 2 g each, what strength HCl should be used in titrating the excess $Ba(OH)_2$ so that each milliliter of HCl corresponds to 0.03 per cent C?

34. In the analysis of steel by the volumetric procedure described in the text, solutions of $Ba(OH)_2$ and HCl are prepared which are of the same normality and 1 ml of HCl neutralizes 0.0053 g of Na_2CO_3 in the standardization. In the analysis 80 ml of $Ba(OH)_2$ is used. What weight of steel should be taken so that the per cent carbon is found by the expression $(80 - n)/120 =$ per cent C, where n is the number of milliliters of HCl required for the excess $Ba(OH)_2$?

CHAPTER XVIII

NICKEL, CHROMIUM, AND VANADIUM IN IRON AND STEEL

Nickel is added to steel to increase the strength and elastic limit without reducing the ductility. It forms with iron a complete series of homogeneous solid solutions (mixed crystals). Nickel is sometimes used alone as alloying ingredient of steel in quantities up to 5 per cent but is also used together with chromium for making heat-resisting and corrosion-resisting materials; usually about 2 parts of nickel to 1 of chromium are used. Chromium imparts hardness and resistance to corrosion. Vanadium can serve both as a deoxidizing and as an alloying constituent. Usually a cheaper deoxidizing agent is used although it has been claimed that a little ferrovanadium helps greatly to produce sound ingots. Chrome-vanadium steels are used extensively in automobile parts which require a high elastic limit and great ductility.

Nickel can be separated from ferric ions in a number of different ways: 1. A fair separation can be accomplished by pouring the solution into an excess of ammonium hydroxide solution. The iron is precipitated as ferric hydroxide, and the nickel stays in solution as nickel-ammonia complex ions; the presence of ammonium salt also represses the ionization of ammonium hydroxide so that the solubility product of nickelous hydroxide is not reached even when insufficient ammonia is present to form the pale blue complex ions. The separation accomplished with ammonia and ammonium salt is never perfect; the ferric hydroxide adsorbs a little nickel even after the precipitation has been repeated several times.

2. Ferric ions can be precipitated by the so-called basic acetate method. By boiling the dilute acetic acid solution in the presence of excess sodium acetate, the ferric ions are precipitated completely as basic ferric acetate but the solution does not become sufficiently basic to precipitate nickelous hydroxide. Ferric ions are precipitated by hydrolysis at pH 4.3, but basic nickelous salts are not formed at $p\text{H} < 6.7$. This separation is good but somewhat tedious. If a large sample is taken for analysis, the basic ferric acetate precipitate is very bulky, slow to filter, and hard to wash.

3. Ferric ions can be precipitated by adding barium carbonate to the cold dilute solution. This method was formerly used a great deal in qualitative analysis, but the ferric hydroxide precipitate is bulky and slow to filter.

4. Rothe's ether separation (cf. p. 303) can be used to remove the greater part of the ferric chloride from a solution, and the problem of separating a small quantity of iron from nickel by one of the above methods is not so difficult as when much iron is present.

5. Ferric ions can be precipitated completely by ammonia without dragging down nickel if the slightly acid solution is treated with just a little more KCN than is sufficient to form $K_2[Ni(CN)_4]$ and is then poured into a dilute solution of NH_4OH.

6. Cupferron, $C_6H_5(NO)NONH_4$, serves to precipitate iron, vanadium, titanium, and zirconium from an acid solution. The excess reagent remains in solution with the nickel and has to be taken into consideration.

Correct determinations of nickel in steel can be accomplished without bothering to remove the ferric ions by any of the above methods. The two most useful methods for determining nickel in steel are the gravimetric determination as the salt of dimethylglyoxime, $CH_3{\cdot}CNOH{\cdot}CNOH{\cdot}CH_3$, and the volumetric determination by titration with potassium cyanide solution. If tartaric acid or other substance that forms complex ions is added to prevent precipitation of ferric ions upon making the solution ammoniacal, either determination can take place without removing the iron from the solution.

Very accurate nickel results can be obtained by the electrolysis of strongly ammoniacal nickel sulfate solutions containing considerable ammonium sulfate, but the gain in accuracy in steel analysis is not commensurate with the greater labor required to remove the iron before the electrolysis. In the analysis of alloys rich in nickel, the electrolytic method has the advantage that a larger sample can be used, but the idea is fallacious that better results are likely to be obtained by dissolving a dimethylglyoxime precipitate in acid, oxidizing the organic material, and then carrying out an electrolysis than by weighing the nickel dimethylglyoxime precipitate.

Determination of Nickel in Steel as the Salt of Dimethylglyoxime

Dimethylglyoxime, $CH_3{\cdot}CNOH{\cdot}CNOH{\cdot}CH_3$, was recommended by L. Tschugaeff[1] as a reagent for nickel and used by K. Kraut[2] for detecting the presence of traces of nickel in ashes. O. Brunck[3] and others have also studied the reaction and have found it to furnish a most rapid and accurate method for the exact estimation of nickel either by itself or in the presence of cobalt, zinc, and manganese. If the solution contains tartaric acid enough to prevent the precipitation of iron by ammonia, the nickel in a sample of nickel steel can be determined accurately within 2 hours and without the removal of any other metal.

When a dilute, neutral solution of a nickel salt is treated with an alcoholic solution of dimethylglyoxime, a red, crystalline precipitate of nickel dimethylglyoxime is formed.

$$NiCl_2 + \underset{\text{Dimethylglyoxime}}{2(CH_3)_2C_2(NOH)_2} = \underset{\text{Nickel dimethylglyoxime}}{[(\mathbf{CH}_3)_2\mathbf{C}_2\mathbf{NOH{\cdot}NO}]_2\mathbf{Ni}} + 2HCl$$

The salt is soluble in mineral acids so that precipitation is incomplete because of the acid set free in the reaction. It becomes quantitative, however, if the mineral acid is neutralized by ammonia or if sodium acetate is added, whereby the mineral acid is replaced by acetic acid in which the precipitate is practically insoluble. Large quantities of ammonium salts or of alkali acetate do no harm, but an excess of ammonia tends to retard the formation of the precipitate. The precipitate is distinctly soluble in absolute alcohol, but only traces dissolve in 50 per cent alcohol, and in more dilute alcohol it is even less soluble. When thrown down in the cold or in the presence of much free ammonia the precipitate is very voluminous and hard to filter.

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[1] *Z. anorg. Chem.*, **46**, 144 (1905); *Ber.*, **38**, 2520 (1905).

[2] *Z. angew. Chem.*, **19**, 1793 (1906); *ibid.*, 20, 1844 (1907).

[3] *Ibid.*, **20**, 834 (1907), *Stahl u. Eisen*, 28, 331.

Procedure. Dissolve 0.5 of steel in 20 ml of 6 N hydrochloric acid. To the resulting solution add 5 ml of concentrated nitric and boil 2 minutes to oxidize iron. Dilute to 100 ml, and filter if there is any perceptible residue. Add 3 g of tartaric acid, and make the solution ammoniacal and then barely acid with acetic acid. Dilute to 300 ml, heat nearly to boiling, and treat with 20 ml of a 1 per cent alcoholic solution of dimethylglyoxime.[1] Finally make slightly ammoniacal, adding enough ammonia to make the solution barely smell of this reagent. Allow the solution to stand in a warm place for 15 minutes and then cool for half an hour or longer. Finally filter the solution through a Gooch or Munroe crucible, wash thoroughly with hot water, dry at 105° for 90 minutes, and weigh as $Ni(C_4H_7N_2O_2)_2$. To the filtrate add 5 ml more of dimethylglyoxime reagent and make sure that the solution is barely alkaline. There should be no further precipitation.

By this method the nickel in a sample of steel can be determined within about 2 hours. The results are accurate, but lower than those sometimes obtained in practice when the cobalt is determined with the nickel. The precipitate is too voluminous to handle easily when the solution contains more than 0.1 g of nickel.

The above procedure has been found to give excellent results with students over a period of about 25 years. The sample analyzed should not contain more than about 0.04 g of nickel. Good results, however, have been obtained with nearly pure nickel when the HCl solution of 0.15 g of the metal was diluted to a definite volume, the solution mixed, and an aliquot of one-fifth taken for the precipitation.

In nearly every set of directions given since 1907, emphasis is placed on avoiding excess of the reagent because of the solubility of the precipitate in alcohol. As a matter of fact, however, the principal difficulty caused by the use of too much reagent is the precipitation of white needles of dimethylglyoxime itself; the reagent is much less soluble in water than in alcohol. The deposited crystals of dimethylglyoxime can be dissolved by washing with hot, dilute ammonia solution. Washing the precipitate with a *little* hot 50 per cent alcohol has been found to be more efficient, and by this treatment but very little of the nickel precipitate is dissolved.

It has been thought that the electrolytic determination of nickel is more accurate, and some directions call for dissolving the dimethylglyoxime precipitate in acid, destroying the organic matter by adding HNO_3 and evaporating with H_2SO_4, and finally depositing the nickel electrolytically from a strongly ammoniacal solution. A skilful analyst can obtain good results in this way, but for students, direct weighing of the precipitate of nickel dimethylglyoxime is better.

Some chemists prefer to titrate the nickel. Wash the nickel dimethylglyoxime precipitate on a paper filter with 3 portions of cold water, dissolve it in 6 N HNO_3, and wash the filter with hot water. Boil the solution 2 minutes, cool, add 5 ml of a solution containing 1 g citric acid, 1.35 g $(NH_4)_2SO_4$, and 1 ml of concentrated ammonia. Neutralize and titrate as described on p. 284.

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[1] The volume of the alcoholic solution should never be more than half that of the nickel solution, as the precipitate is slightly soluble in alcohol. About 0.4 g of the glyoxime should be used for each 0.1 g of nickel. A deep red color in the solution shows that ferrous iron is present.

Determination of Nickel by Potassium Cyanide[1]

This method, which permits the volumetric estimation of nickel with speed and accuracy even in the presence of iron, manganese, chromium, zinc, vanadium, molybdenum, and tungsten, depends upon the fact that nickel ions react with potassium cyanide in slightly ammoniacal solution, to form a complex anion $[Ni(CN)_4]^{--}$:

$$Ni(NH_3)_6Cl_2 + 4KCN = K_2[Ni(CN)_4] + 6NH_3 + 2KCl$$

If the solution of the nickel salt contains a precipitate of silver iodide, produced by adding a known amount of silver nitrate and a few drops of potassium iodide solution, the turbidity will not disappear until all the nickel has entered into reaction with the potassium cyanide.

$$\mathbf{AgI} + 2CN^- = K[Ag(CN)_2] + I^-$$

The titration is finished by adding just enough more silver nitrate to cause the precipitate of silver iodide to reappear.

$$I^- + Ag^+ = \mathbf{AgI}$$

Requirements. 1. A *nickel solution* of known content. Dissolve 10 g of pure nickel in 125 ml of 6 *N* nitric acid, boil off the nitrous fumes, and dilute with water to 1 l at 20°.

2. A *silver nitrate solution.* Dissolve 5 g of silver nitrate in water and dilute to 1 l.

3. A *potassium cyanide solution.* Dissolve 15 g of pure potassium cyanide and dilute to 1 l.

4. A *potassium iodide solution.* Dissolve 10 g of potassium iodide in 100 ml of water.

Standardization of the Potassium Cyanide Solution. To 10 ml of the nickel solution, accurately measured with a pipet, add ammonium hydroxide in slight excess, dilute to 100 ml, and add 6 drops of potassium iodide solution and about 1 ml of silver solution from a buret, noting the reading of the buret before adding the silver solution. From another buret, slowly run in potassium cyanide solution, with constant stirring, until the silver iodide precipitate dissolves. Then very carefully add silver nitrate solution until a permanent turbidity is formed and dissolve this by the careful addition of more potassium cyanide solution. Continue in this way until 2 drops of the potassium cyanide solution suffice to dissolve the last silver iodide turbidity produced by adding the silver nitrate solution. Since the potassium cyanide solution decomposes slowly, this titration must be made every day that the solution is used.

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[1] Cf. Campbell and Andrews, *J. Am. Chem. Soc.*, **17**, 126 (1895); Moore, *Chem. News*, **72**, 92 (1895); Goutal, *Z. angew. Chem.*, **1898**, 177; Brearley and Jarvis, *Chem. News*, **78**, 177 and 190 (1898); Johnson, *J. Am. Chem. Soc.*, **29**, 1201 (1907); Campbell and Arthur, *ibid.*, **30**, 1116 (1908); and Grossmann, *Chem. Ztg.*, **32**, 1223 (1908).

Next determine the relative strengths of silver solution and potassium cyanide solutions. From a buret, add 30 ml of the potassium cyanide solution, neutralize with ammonia, dilute, add potassium iodide, and titrate in exactly the same way as just outlined.

From this last titration in which a ml of silver nitrate were found equal to b ml of potassium cyanide, 1 ml of $AgNO_3$ solution = b/a ml of KCN solution. If T ml of potassium cyanide and t ml of silver nitrate were used in the titration of 10 ml of nickel solution (= 0.1 g Ni), then

$$1 \text{ ml of KCN solution} = \frac{0.1}{T - (b/a)t} \text{ grams Ni}$$

Determination of Nickel in Solutions of Nickel Salts

Procedure. To 100 ml of solution containing approximately 0.1 g of nickel, add ammonium hydroxide[1] and continue exactly as in the above standardization with pure nickel solution.

F. Sutton[2] states that, instead of working with two solutions, equally reliable results can be obtained by using a potassium cyanide solution to which a little silver nitrate has been added. Thus, to the above solution of potassium cyanide there may be added about 0.50 g of silver nitrate which is first dissolved in water by itself. If this solution is used for titrating a nickel solution to which potassium iodide solution has been added, a precipitate of silver iodide is formed at once which increases at first on adding the potassium cyanide-silver nitrate solution until all the nickel is converted into potassium nickelocyanide, but the precipitate eventually disappears upon the further addition of the solution.

Remarks. Instead of titrating the potassium cyanide against a known nickel solution, the standardization may be accomplished with 0.1 N silver nitrate solution. In this case it is best to take as end point the formation of a slight turbidity on adding silver nitrate, rather than the dissolving of the precipitate with potassium cyanide. One milliliter of 0.1 N silver nitrate solution = 0.01302 g of KCN = 0.002934 g of Ni.

The method can be carried out in the presence of most of the other elements of the ammonium sulfide group. If a clear solution is not obtained on adding ammonium hydroxide, the addition of ammonium chloride sometimes helps. If copper is present in amounts not exceeding 0.4 per cent, the copper will replace almost exactly three-quarters of its weight of nickel. If chromium is present, the dark color due to the presence of chromic salts may be obviated by adding to the original sulfuric acid solution a 2 per cent solution of potassium permanganate until a slight permanent precipitate of manganese dioxide is obtained, whereby the chromium is oxidized to chromic acid. Filter the solution, concentrate in a 400-ml beaker to about 60 ml, then treat with sodium pyrophosphate, as described below. The method is not applicable in the presence of considerable cobalt, which is betrayed by the dark color assumed by the solution upon the addition of potassium cyanide, but when the amount of the latter does not exceed one-tenth the amount of nickel present, the titration can be carried out successfully and the results represent the amount of nickel and cobalt present.

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[1] If the addition of ammonia does not give a clear solution, a few cubic centimeters of ammonium chloride solution should be added.

[2] *Volumetric Analysis*, 8th edition, p. 252.

Zinc causes trouble unless alkali pyrophosphate is added. The titration can be carried out in the presence of aluminum, iron, and manganese if citric or tartaric acid or sodium pyrophosphate is added.

The temperature of the solution should not be much above 20°, for in hot solutions the results are not concordant. The quantity of ammonia present should not be too great, because there is a tendency for ammonia to impede the reaction if more than a slight excess is present. Potassium cyanide containing sulfide cannot be used; the reagent should be the purest obtainable. The results are accurate. The method has been modified so that it can be used to advantage for the determination of nickel in nickel steel.

The following procedure is not applicable in the presence of copper or cobalt, both of which react like nickel with KCN, or in the presence of tungsten, which gives a turbidity of hydrated WO_3 that interferes with the end point.

Determination of Nickel in Nickel Steel

Dissolve 1 g of steel in a casserole with 20 ml of 6 N nitric acid, adding a little hydrochloric acid if necessary. (If much chromium is present use 20 ml of $9N$ H_2SO_4 and, later, 5 ml of concentrated nitric acid to dissolve carbides.) After the steel has dissolved, add 10 ml of 15 per cent $(NH_4)_2S_2O_8$ solution and boil 5 minutes. Then filter if necessary. Cool, and, to prevent precipitation of $Fe(OH)_3$ on neutralization, add 10 ml of a solution made by dissolving 20 g of citric acid, 27 g $(NH_4)_2SO_4$, and 20 ml of concentrated NH_4OH in 80 ml of water. Cool to room temperature, and add 6 N ammonia until the solution assumes a greenish tint and is basic to litmus. Cool the clear solution to room temperature and dilute to 200 ml with cold water; carefully measure out from a buret about 0.5 ml of the standard silver nitrate solution and add 2 ml of the potassium iodide. Titrate with potassium cyanide until the precipitate of silver iodide has disappeared, and finish by adding just enough more of the silver nitrate to cause the formation of a slight turbidity again.

Chromium in Steel

Chromium, when present as trivalent chromic cations, behaves like ferric iron toward many reagents. Practically all methods for determining chromium in iron and steel are based upon its oxidation to the positive valence of 6 as chromic acid, dichromate, or chromate. Small quantities of chromium can be determined colorimetrically, but quantities larger than a few hundredths of 1 per cent are usually determined by adding a measured volume of reducing agent, usually acid ferrous sulfate solution, and titrating the excess with potassium permanganate solution. A great many different methods have been proposed for carrying out the oxidation, but treatment with ammonium persulfate in the presence of silver ions as catalyst has been found most convenient. If vanadium is present, it can be determined in the same solution after the chromium.

Determination of Chromium and Vanadium in Alloy Steel[1]

In this procedure the manganese, chromium, and vanadium are first obtained in the bivalent, trivalent, and quadrivalent states respectively by dissolving in acid. By the action of persulfate in the presence of silver salt as catalyzer, the bivalent manganese is oxidized to the valence of 7, the trivalent chromium to the valence of 6, and the quadrivalent vanadium to the valence of 5. By the addition of a limited quantity of chloride, the permanganic acid is reduced to manganous salt and the excess persulfate is removed by boiling. The chromic acid is then reduced to chromic salt by a measured quantity of ferrous solution, and the excess titrated with permanganate. The chromium content corresponds to the amount of ferrous salt required. The vanadium, to be sure, is reduced to vanadyl salt by the ferrous iron but is again oxidized to vanadic acid by the permanganate so that it affects the analysis only by making the end point a slow one.

After the titration, all manganese is present as manganous salt, all chromium as chromic salt, and all vanadium as vanadate. Another portion of ferrous salt serves to reduce the vanadium to quadrivalent vanadyl salt. The excess ferrous iron can be oxidized by stirring with persulfate solution without oxidizing the vanadium, and the vanadyl salt can be titrated with permanganate.

The important chemical reactions involved can be expressed by the following equations:

Oxidation with persulfate in the presence of Ag^+ ions:

$$2Cr^{+++} + 3S_2O_8^{--} + 8H_2O \rightarrow 2H_2CrO_4 + 6SO_4^{--} + 12H^+$$
$$2VO^{++} + S_2O_8^{--} + 4H_2O \rightarrow 2HVO_3 + 2SO_4^{--} + 6H^+$$
$$2Mn^{++} + 5S_2O_8^{--} + 8H_2O \rightarrow 2HMnO_4 + 10SO_4^{--} + 14H^+$$

Removal of the catalyzer and reduction of $HMnO_4$:

$$Ag^+ + Cl^- \rightarrow AgCl$$
$$2HMnO_4 + 14H^+ + 10Cl^- \rightarrow 2Mn^{++} + 8H_2O + 5Cl_2$$

Reduction with $FeSO_4$:

$$Cr_2O_7^{--} + 6Fe^{++} + 14H^+ \rightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O$$
$$HVO_3 + Fe^{++} + 3H^+ \rightarrow VO^{++} + Fe^{+++} + 2H_2O$$

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[1] Procedure based on *Methods of the Chemists of the United States Steel Corporation.*

Titration with $KMnO_4$:

$$5Fe^{++} + MnO_4^- + 8H^+ \rightarrow 5Fe^{+++} + Mn^{++} + 4H_2O$$
$$5VO^{++} + MnO_4^- + 6H_2O \rightarrow 5HVO_3 + Mn^{++} + 7H^+$$

Reduction with $FeSO_4$ the second time:

$$HVO_3 + Fe^{++} + 3H^+ \rightarrow VO^{++} + Fe^{+++} + 2H_2O$$

Removal of excess $FeSO_4$ the second time:

$$2Fe^{++} + S_2O_8^{--} \rightarrow 2Fe^{+++} + 2SO_4^{--}$$

Final titration:

$$5VO^{++} + MnO_4^- + 6H_2O \rightarrow 5HVO_3 + Mn^{++} + 7H^+$$

Procedure. Weigh out 2 g of sample, or less if more than 2 per cent of chromium is present, into a 600-ml beaker, and cover it with a mixture of 45 ml water, 10 ml concentrated sulfuric acid, and 5 ml of phosphoric acid, *d* 1.7. Heat until there is no further action, add 5 ml of concentrated nitric acid, and boil to decompose carbides and oxidize the iron. (If carbides resist this treatment, as shown by considerable dark-colored residue, or tungsten is present as shown by a yellow residue of WO_3, evaporate until salts begin to separate out, dilute with 50 ml of water, add 10 ml of concentrated HNO_3, and again evaporate.) Add 200 ml of water, filter, and wash the residue with water. To the filtrate add 10 ml of 0.1 *N* silver nitrate, heat nearly to boiling, and add slowly while stirring 20 ml of freshly prepared 15 per cent ammonium persulfate solution. If a permanganate color does not develop from the manganese in the steel, heat again and add more silver nitrate and more persulfate. Then boil 8–10 minutes to decompose the excess persulfate, add 2 ml of 6 *N* hydrochloric acid, and heat 5 minutes after the permanganate color, or any precipitated manganese dioxide, has disappeared. Dilute to 400 ml, add 25 ml of 0.1 *N* ferrous ammonium sulfate solution from a pipet, and test a drop of the solution on a white porcelain spot plate with a freshly prepared solution of potassium ferricyanide. If the blue test is not obtained, add another portion of ferrous salt. Titrate the excess with 0.1 *N* permanganate until the pink end point persists after stirring for 1 minute.

In this analysis a perceptible excess of permanganate is required because of the dilution and the color of the chromic salt. To allow for this error, assume that the milliequivalent of chromium is 0.01744 instead of the theoretical value. The end point is a little difficult because of the slow rate of oxidation of the vanadium in cold, dilute solutions.

Determination of Vanadium. After the chromium determination, add 5 ml of standard ferrous ammonium sulfate solution from a pipet. Stir and test a drop of the solution for ferrous iron with fresh ferricyanide solution, adding another pipetful of ferrous salt if necessary. Add 8 ml of 15 per cent ammonium persulfate solution and stir 1 minute to oxidize the excess of ferrous salt. Then titrate with permanganate till the end point persists after 1 minute's stirring. In this case, the vanadium is titrated directly and 1 ml of 0.1 N permanganate oxidizes 0.005096 g of vanadium. The error due to dilution and color of the chromic ions is positive. From the percentage of vanadium found, subtract 0.02 plus 0.018 times the percentage of chromium in the sample.

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35. If 0.8 g of the nickel salt of dimethylglyoxime is heated in a current of air so that all the hydrogen is changed to water and the gas then led through a $CaCl_2$ tube, what will be the gain in weight?

36. A sample of nickel ore yields 0.267 g of Ni and Co by electrolysis and 0.94 g of precipitate with glyoxime. Find the percentage of Ni and of Co if the sample weighed 0.89 g.

37. A 2-g sample of steel is analyzed for chromium. A certain volume of 0.1500 N $FeSO_4$ solution is added, and the excess is titrated with 0.1000 N $KMnO_4$, requiring 30.00 ml. If the sample contained 0.50 per cent Cr, what volume of $FeSO_4$ was added?

38. From the following data compute the percentage of Cr in a sample of steel. Weight of sample = 1.850 g. After oxidation with $KMnO_4$ and removal of the excess reagent, 150 ml of 0.0800 N ferrous solution is added and the solution then reacts with 14.00 ml of 0.0900 N $KMnO_4$.

39. In the determination of chromium the sample of steel weighed 2.52 g, and, after conversion of all the chromium to chromic acid, 50.0 ml of 0.110 N ferrous solution was added and the excess titrated with $KMnO_4$ solution (1 ml $KMnO_4$ = 0.00500 g of $H_2C_2O_4 \cdot 2H_2O$). If the steel contained 0.49 per cent Cr, what volume of $KMnO_4$ solution was needed in the titration?

40. Given 0.080 N $KMnO_4$ and 0.090 N ferrous solution, what weight of steel should be taken for analysis when, after reduction with 50 ml of the ferrous solution and titration with n ml of $KMnO_4$,

$$\text{Per cent Cr} = \frac{56.25 - n}{5}$$

41. In the determination of chromium with 0.103 N $FeSO_4$ solution and 0.0850 N $KMnO_4$, it is desired to take a weight of sample such that by subtracting the volume of permanganate from a *certain number* and dividing by 20, the percentage of chromium is obtained. Find the weight of sample and the *number* when 100 ml of ferrous solution is used.

42. In the determination of chromium in s g of steel, p g of pure $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ was used which provided more than sufficient Fe^{++} to reduce all the CrO_3 formed. If the per cent Cr = $(50p - n)/8$, find the weight of sample and normality of the $KMnO_4$ used.

Ans. 7.07 g, 0.05102 N.

43. If 0.0850 g of pure $Na_2V_4O_9$ could be reduced to a state such that 43.14 ml of $KMnO_4$ (40 ml $KMnO_4$ oxidizes 30 ml $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$ solution which is

0.08 *N as an acid*) would be required to oxidize it back to the quinquevalent state, find the valence of the vanadium in the reduced state and the oxide to which it corresponds.

44. A sample of steel which weighed 0.800 g was analyzed for Ni by the titration method. Calculate the per cent Ni present. Used 0.0050 g $AgNO_3$, 1.002 g KI, and 16.0 ml of KCN (1 ml = 0.01699 g $AgNO_3$).

45. If an alloy steel contains 0.50 per cent Mn, 3.52 per cent Cr, and 0.97 per cent V, calculate the minimum weights of $(NH_4)_2S_2O_8$ required to convert the Mn to $HMnO_4$, the Cr to H_2CrO_4, and the V to HVO_3 in a sample which weighs 2.0 g and has been dissolved in acid to give Mn^{++}, Cr^{+++}, and VO^{++}.

46. In the volumetric determination of chromium does the color of the chromic irons tend to cause positive or negative error in the percentage of Cr found?

47. In the volumetric determination of nickel, does the presence of copper and cobalt cause positive or negative errors?

CHAPTER XIX

SULFUR, SILICON, AND TUNGSTEN IN STEEL

SULFUR

Sulfur occurs in irons and steels chiefly as sulfide of iron, manganese, or titanium and represents impurity or, in other words, enclosed slag. Manganese sulfide is the most commonly occurring form, and iron sulfide is formed only when more sulfur is present than there is manganese to combine with it. The occurrence of titanium sulfide is rare.

The effect of sulfur present as iron sulfide is to make the metal " red short," i.e., brittle at the forging temperature. The effect is overcome by the addition of manganese, but in some cases the manganese sulfide becomes rolled out into filaments and these are brittle and cause weakness. Breaks in the metal often start where there is some manganese sulfide; this compound is easily identified in etched specimens by its characteristic dove color under the microscope. The maximum permissible sulfur content is usually specified among the requirements of a given kind of steel. Most steels contain less than 0.05 per cent, but in some samples of stainless steel it may run as high as 0.45 per cent.

Sulfur can be determined colorimetrically by treating the steel with acid and causing the escaping gases to pass through a cloth which has been moistened with cadmium acetate solution. The estimation of the sulfur content is then based on a comparison of the tint produced with tints produced similarly with steels containing known quantities of sulfur.

In ordinary routine work, sulfur in steel is usually determined by the so-called *evolution method.* The sample is treated with hydrochloric acid, and the escaping hydrogen sulfide is collected in some suitable absorbent, such as an ammoniacal solution of zinc sulfate or of cadmium chloride. The hydrogen sulfide is liberated again by treatment with acid and oxidized at once to free sulfur either by adding a measured volume of iodine directly, or indirectly by adding a measured volume of potassium permanganate or potassium iodate solution together with an excess of potassium iodide, whereby a known quantity of iodine is liberated. Finally the excess iodine is titrated with sodium thiosulfate.

When great accuracy is desired, it is best to oxidize the sulfur to sulfate and precipitate this as barium sulfate which can be ignited and weighed. Much has been written about the difficulty of obtaining pure precipitates of barium sulfate, especially in the presence of considerable ferric salt. To overcome this difficulty: (1) it has been proposed to remove the greater part of the iron as ferric chloride by shaking the HCl solution with ether. This method gives excellent results, but the procedure is rather long and work with ether is not altogether pleasant. (2) Meineke recommended treating the sample of steel with a slightly acid solution of cupric and potassium chlorides. This leaves the sulfur in the residue which is filtered off, oxidized by HNO_3 and $KClO_3$, and eventually precipitated as $BaSO_4$. (3) Bamber, on the other hand, evaporated the HNO_3 solution of the steel to dryness after adding some alkali salt, and then, by ignition over an alcohol flame, the ferric nitrate was decomposed and made insoluble in water while the sulfur was left as soluble alkali sulfate. Then, after the addition of acid, the sulfate was determined as barium sulfate in the usual way.

In this book directions will be given for simple methods of carrying out the gravimetric determination and the evolution method.

Gravimetric Determination of Sulfur

Dissolve 4.57 g of steel $(100 \times S)/(3 \times BaSO_4)$ by heating carefully with 50 ml of concentrated HNO_3. If the sample dissolves very slowly, add a little concentrated HCl dropwise at intervals. To the solution add 0.5 g of Na_2CO_3, evaporate carefully to dryness, and bake for 15 minutes on the hot plate. Cool, add 30 ml of concentrated HCl, and repeat the evaporation and baking. Now add 30 ml of concentrated HCl and evaporate to a sirup. Add 5 ml more of HCl, 20 ml of water, and 5 g of 20–30 mesh zinc, free from sulfur. This serves to reduce the iron to ferrous salt which does not interfere as much as $FeCl_3$ does with the precipitation of all SO_4^{--} as pure $BaSO_4$. Heat on the water bath until all the ferric ions are reduced and the evolution of hydrogen has nearly ceased. Filter and wash with about 75 ml of 0.25 N HCl, added in small portions. Heat to about 70°, and add 10 ml of 10 per cent barium chloride solution. Allow to stand over night. Filter through an ashless filter; wash six times with hot N HCl and then with hot water until free from chloride. Ignite and weigh the $BaSO_4$. Run a blank on all the reagents going through all the above operations in exactly the same way. To find the percentage of sulfur, multiply the weight of the precipitate of $BaSO_4$ in grams by 3.

Evolution Method for Sulfur

Transfer 5 g of steel borings to a 250-ml flask which is fitted with a rubber stopper carrying a thistle tube that extends nearly to the bottom of the flask and a Kjeldahl distilling bulb which ends just below the surface of the stopper (Fig. 44). This bulb acts as a splash trap. Connect the outside end of the bulb with glass tubing that reaches nearly to the bottom of a 200-ml Erlenmeyer flask. Connect the latter with a second Erlenmeyer flask. In each of the Erlenmeyer flasks place 50 ml of water and 10 ml of either of the following ammoniacal absorbents.

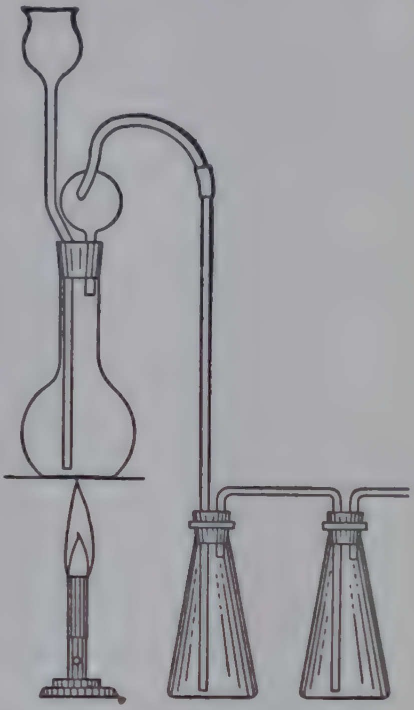

FIG. 44.

Ammoniacal Zinc Sulfate. Dissolve 20 g of $ZnSO_4 \cdot 7H_2O$ in 100 ml of water, and to the solution add an equal volume of concentrated ammonium hydroxide. Filter after standing over night.

Ammoniacal Cadmium Chloride. Dissolve 12 g of $CdCl_2 \cdot 2H_2O$ in 150 ml of water and to the solution add 60 ml of concentrated ammonium hydroxide. Filter if not clear.

Pour 80 ml of 6 N HCl through the thistle tube of the evolution flask and heat so that there is a rapid and steady evolution of gas. When all the steel has dissolved, boil for 30 seconds, but never long enough to cause much HCl to pass over into the other flasks. The first flask should contain all the sulfur of the steel as white ZnS or as yellow CdS. The second flask is used merely to make sure that no H_2S escapes unabsorbed. Filter off the sulfide precipitate, and wash out the flask twice with dilute NH_4OH (approximately 0.5 N). Transfer the filter and precipitate to a beaker, and cover with 300 ml of water. Rinse out the delivery tubing, where there is any sulfide, with 50 ml of N HCl, and add this solution to the liquid in the beaker containing the precipitate. At once add a measured volume of standard iodine solution (10 ml of 0.05 N solution is usually sufficient and should be added from a pipet), and after a few minutes titrate the excess iodine with sodium thiosulfate solution to a starch end point (see p. 128).

Unless the relative strengths of the two solutions have been checked recently, add 10 ml of the iodine solution from a pipet to 300 ml of water to which 5 ml of concentrated HCl has been added and titrate with thiosulfate to a starch end point.

In this analysis, the milliequivalent weight of sulfur is 0.016 g. Standardize the solutions by any method described on pp. 130–133.

Most cast irons do not give up all their sulfur by this method of analysis. The values are nearer the truth if the sample is annealed as follows: Wrap 5 g of sample in two 11-cm filter papers so that all the metal is under at least 3 thicknesses of paper. Place in a 25-ml porcelain crucible, cover with a well-fitting lid, and heat 30–40 minutes at about 750°. Cool slowly, and transfer the charred paper and steel to the evolution flask. With high-silicon irons, heat the acid rapidly to boiling and then allow to simmer.

SILICON

Silicon exists in cast irons and steels chiefly as a solid solution of Fe_2Si in iron. In wrought iron and in some steels, a little silicate of Fe or Mn may be present, such as $Mn_2Si_3O_8$; this really represents enclosed slag. The compound FeSi has also been identified in Fe-Si alloys. In cast irons, the silicon has a marked effect in causing the breaking down of cementite, Fe_3C, into Fe and graphite. With increasing Si content, the graphite increases, but this effect is counterbalanced by the effect of S so that, roughly speaking, a given percentage of S neutralizes a definite percentage of Si.

Although Si enters into salts as silicate ion and not as Si^{++++} ions, the free element and its compounds with iron are oxidized very easily so that decomposition with any acid will cause oxidation of the Si to the quadrivalent state with evolution of hydrogen gas. There is, therefore, no loss of volatile silicon hydride when a sample of steel is dissolved in hydrochloric or sulfuric acid. If, however, nitric acid or other oxidant is used, the more powerful oxidizing agent is reduced without any evolution of hydrogen.

$$FeSi + 2H^+ + 3H_2O \rightarrow Fe^{++} + H_2SiO_3 + 3H_2\uparrow$$

$$Fe_2Si + 4H^+ + 3H_2O \rightarrow 2Fe^{++} + H_2SiO_3 + 4H_2\uparrow$$

$$3Fe_2Si + 28H^+ + 10NO_3^- \rightarrow 6Fe^{+++} + 10NO\uparrow + 3H_2SiO_3 + 11H_2O$$

In these reactions the product is really $SiO_2{\cdot}xH_2O$ rather than exactly H_2SiO_3.

The following method[1] is excellent for the determination of silicon. Perchloric acid is used instead of sulfuric acid[2] because anhydrous perchlorates are easily soluble and there is no difficulty in dissolving the salts after the silica has been dehydrated. Chromium is oxidized to chromic acid and remains in solution. The chief precautions are to add sufficient perchloric acid to keep the mixture liquid after the nitric acid has been expelled and to *boil* at least 15 minutes at this stage in the analysis.

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[1] Willard and Cake, *J. Am. Chem. Soc.*, **42**, 2208 (1920).

[2] T. M. Drown, *Trans. Am. Inst. Mining Eng.*, **7**, 346 (1878–79).

Procedure. Treat 2.236 g of sample (5 times the factor weight) with 40 ml of 6 N HNO_3 in a 400-ml covered beaker. When the sample is entirely decomposed, rinse and remove the watch-glass cover and add 40 ml of 60–70 per cent $HClO_4$. Evaporate to fumes of $HClO_4$. Replace the watch glass on the beaker, and heat so that the $HClO_4$ condenses and runs down the sides of the beaker for 15 minutes, but do not allow the contents of the vessel to become pasty or solid. Cool somewhat, and dilute with 125 ml of hot water. Stir until the salts have dissolved, and crush any lumps with a glass stirring rod. Filter and transfer all the residue to an ashless filter paper with the aid of 0.6 N HCl, scrubbing the beaker with a rubber policeman. Wash alternately with 5-ml portions of hot 0.6 N HCl and of hot water until all the iron salts have been removed. The washing must be done carefully as residual $HClO_4$ may cause loss of material in the subsequent ignition of the precipitate. Transfer the paper and residue to a weighed platinum crucible, and ignite slowly and carefully until all the carbon is gone. Cool in a desiccator, and weigh the *impure* SiO_2. Moisten the residue with 18 N H_2SO_4 and add (without measuring) about 5 ml of HF. Heat inside an air bath until all H_2SO_4 is expelled, and then heat the crucible strongly over a free flame. Cool in a desiccator and weigh. The loss in weight represents the SiO_2, and, when the above weight of sample is taken, this loss multiplied by 20 gives the percentage of Si present.

TUNGSTEN

Modern alloy steels often contain from 0.5 to 20 per cent of tungsten. It may be present as WC or as Fe_2W. In mild steel, tungsten up to 1 per cent has little effect upon the mechanical properties, but " high-speed " steels containing 13–18 per cent tungsten, 2.5–5 per cent chromium, 0.6–0.7 per cent carbon, and up to 1 per cent vanadium are characterized by their ability to be worked at a speed 3 to 5 times as great as that at which plain carbon steels can be worked, and these high-speed steels retain their hardness even at a red heat. The steel can be hardened at a white heat which would ruin a plain carbon steel. Probably double carbides of Cr and W are formed in the steel and remain in it on rapid cooling and to some extent on slow cooling.

After thorough oxidation of a sample of steel by treatment with acid and an oxidizing agent, the tungsten is obtained as a hydration product of yellow WO_3 (tungstic acid anhydride). This, like silicic acid, is insoluble in water but tends to form colloidal solutions. The problem, therefore, is to oxidize the tungsten to tungstic acid and then to make sure that it is all precipitated together with any silicic acid that may be present. The complete precipitation is aided by adding some cinchonine hydrochloride to the solution; cinchonine is an alkaloid, or weakly basic organic substance of complicated composition. In the following rapid method, the precipitation of the tungstic acid is not quite complete, but this deficiency is compensated by the presence of small quantities of impurities.

Procedure. Treat 1.0 g of the steel in a 400-ml beaker with 50 ml of concentrated HCl, and heat in the covered beaker until all the metal is decomposed. Remove from the heat and add cautiously 5 to 7 ml of concentrated HNO_3. Cover the beaker, and boil for 5 minutes to oxidize all the iron and convert the tungsten to yellow tungstic acid. Remove from the heat, wash the under part of the watch glass and the sides of the beaker with hot water, dilute to 75–100 ml, and filter through a 9-cm ashless filter containing some filter-paper pulp made from ashless filters. Wash the precipitate alternately, three times each, with 10-ml portions of hot 6 *N* HCl and hot water, and finally with four similar portions of hot water. Transfer the paper and precipitate to a weighed platinum crucible, ignite, and weigh. Treat the impure WO_3 with sulfuric and hydrofluoric acids (see p. 293) to volatilize SiO_2, and call the residue WO_3.

HOME PROBLEMS

48. In the determination of S by the evolution method find the per cent S. Weight of sample = 5.028 g; iodine used = 15.59 ml; thiosulfate solution used = 12.68 ml; 1 ml I_2 = 1.086 ml of thiosulfate solution; 1 ml of thiosulfate solution = 0.005044 g Cu.

49. If all the S in a sample of steel weighing 5 g is converted into H_2S, what weight of CdS will be formed and how many milliliters of 0.08 *N* iodine solution will react with it if the steel contains 0.06 per cent S? What is the ratio of the volume of H_2 to the volume of H_2S evolved, assuming 99.2 per cent Fe?

50. Measured at 30° C and 770 mm pressure, what volume of H_2S will be evolved by HCl from 4 g of ingot iron containing 0.012 per cent S? What is the value of 1 ml of iodine solution in terms of As_2O_3 if 16.00 ml is required to oxidize the S from the above weight of the steel?

51. If a 4-g sample of steel is used for the determination of S, what normality thiosulfate and what normality iodine should be used so that the (ml $I_2 \times 1.2 -$ ml thiosulfate) gives 100 times the per cent S?

52. What weight of sample should be taken so that the milliliters of $Na_2S_2O_3$ used, multiplied by a factor, and subtracted from the milliliters of I_2 used, will be exactly 12 times the per cent S? The concentrations of the solutions used are as follows: One milliliter of the $Na_2S_2O_3$ solution is equivalent to the iodine liberated

when 1 ml of $K_2Cr_2O_7$ (1 ml = 0.004900 g Fe) is treated with KI in acid solution; 1 ml of iodine solution is equivalent to 0.004900 g of As_2O_3. What is the value of the " factor " mentioned above?

53. If a sample of steel contains 3 per cent of Fe_2Si, compute the weight of SiO_2 obtained in the analysis of a sample weighing 3.0 g. Compute the volume of SiF_4 obtained (S.T.P.).

54. A volume of 10.05 ml of SiF_4 at 21° and 740 mm pressure corresponds to what weight of Fe_2Si?

55. If a sample of steel contains 1.2 per cent Si and 0.20 per cent W, calculate the weight of the ignited WO_3 and SiO_2 to be obtained from 3.0 g of steel and the weight of this residue after the usual treatment with HF and H_2SO_4.

56. A sample of steel weighs 5.00 g. The residue of WO_3 and SiO_2, insoluble in acid, weighs 0.0928 g, and after treatment with HF and H_2SO_4 this residue weighs 20 per cent less. Find percentage of W and of Si present.

CHAPTER XX

SOME PRACTICAL METHODS OF ORE ANALYSIS

Among the students of quantitative analysis are always some, particularly the embryo mining engineers, who are specially interested in the analysis of ores. The determination of the precious metals by the so-called dry assay is usually covered by special courses on fire assaying and will not be explained here. In this chapter, practical methods for determining sulfur, zinc, titanium, arsenic, and tungsten will be described. The determination of sulfur is of great importance and has been discussed at great length in the literature. Zinc ores are often analyzed by a method which depends upon titration with potassium ferrocyanide solution, a titration which is capable of yielding very accurate results but requires considerable practice on the part of the beginner. Titanium occurs to a slight extent in almost all rocks, and some titanium products are coming into quite general use; it is desirable that every student should know something about the characteristics of this element. Arsenic and tungsten are not difficult to determine, but these elements can cause a great deal of trouble if a suitable method of analysis is not chosen.

DETERMINATION OF SULFUR IN PYRITE

For this analysis the sulfur is oxidized to sulfate and determined as barium sulfate. The oxidation of the sulfide can take place in the *dry way*, by fusion, or in the *wet way*, in solution.

(*a*) Sodium Peroxide Method[1]

Procedure. Mix 0.5 g of pyrite with 5 g of pure sodium peroxide and 4 g of sodium carbonate in a nickel or iron crucible. Cut an opening in a piece of asbestos board (at least 4 in. square) sufficiently large to allow two-thirds of the crucible to project below the asbestos. The purpose of this shield is to keep the products formed by the combustion of the gas from reaching the mouth of the crucible. Heat the contents of the crucible gently for 10 minutes so that the mass softens and bakes together, and then raise the temperature until the crucible is exposed to the full heat of the Tirrill burner for 20 minutes.

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[1] W. Hempel, *Z. anorg. Chem.*, **3**, 193 (1893); J. Clark, *J. Chem. Soc.*, **63**, 1079 (1893); Höhnel, *Arch. Pharm.*, **232**, 222; C. Glaser, *Chem.-Ztg.*, **18**, 1448; Fournier, *Rev. gén. chim.*, **1903**, 77; List, *Z. angew. Chem.*, **1903**, 414.

Allow the contents of the crucible to cool and place in a small beaker with 150 ml of hot water. When the sodium salts are entirely dissolved, remove the crucible and add 5 ml of a saturated solution of bromine in concentrated hydrochloric acid. The purpose of the bromine is to make sure that the oxidation of the sulfur is complete.[1] It is necessary to add acid, because otherwise the hot sodium hydroxide solution is likely to destroy the filter paper. After heating to boiling, filter the solution and wash the residue of ferric hydroxide free from sulfate.

Carefully neutralize the filtrate with 6 *N* hydrochloric acid, and add 2 ml in excess. Heat the solution till all the bromine is expelled, dilute to 350 ml, heat to boiling, and precipitate with 24 ml of normal barium chloride solution which is diluted to 100 ml and added slowly while stirring vigorously. Filter, wash, ignite, and weigh the barium sulfate precipitate in the usual way (p. 197).

(*b*) Method of G. Lunge

The sample should be finely ground, but it must be borne in mind that rapid grinding in the air may generate enough heat to cause the oxidation of some sulfur so that an appreciable amount escapes as dioxide. Of the fine powder, treat 0.5 g with 10 ml of a mixture consisting of 3 parts nitric acid, *d* 1.42, and 1 part hydrochloric acid, *d* 1.2, in a 300-ml beaker which is covered with a watch glass. At first allow the acid to act upon the pyrite in the cold, but finish by heating upon the water bath. If sulfur separates, oxidize it with a very little powdered potassium chlorate. Transfer the solution to a porcelain evaporating dish and evaporate to dryness on the water bath. Treat the residue with 5 ml of concentrated hydrochloric acid and again evaporate to dryness. Moisten the dry mass now with 1 ml of concentrated hydrochloric acid and 100 ml of hot water, filter through a small filter, and wash the residue first with cold water and then with hot water. To the hot filtrate, if not more than 150 ml in volume, add ammonia till the odor persists and then 30 ml of 3 *N* ammonium hydroxide in excess to prevent the formation of any basic ferric sulfate. Keep at about 70° for 15 minutes. Filter off the ferric hydroxide precipitate and wash with hot water, each time churning up the precipitate, until a volume of about 400 ml is reached. Neutralize the filtrate with hydrochloric acid, using methyl orange as indicator, and add 1 ml of concentrated hydrochloric acid in excess. Heat just to boiling, and add 100 ml of boiling-hot 0.2 N barium chloride solution while stirring vigorously.

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[1] A black residue may denote ferrous sulfide or nickelic oxide. It may be tested for sulfur by dissolving in hydrochloric acid and bromine and adding barium chloride to the diluted solution.

Wash the barium sulfate precipitate 3 times by decantation with boiling water, then transfer to a filter and wash free from chlorides, ignite, and weigh.

To test the ammonia precipitate for sulfur, transfer it from the filter into a beaker by means of a stream of water from the wash bottle and dissolve it by the addition of as little hydrochloric acid as possible. To the resulting solution add an excess of ammonia, filter, and test the filtrate and washings as in the main analysis. Should any barium sulfate be obtained in this way, it should be filtered off and weighed with the main part of the barium sulfate precipitate.

Remark. It is still better to filter the precipitate through a filtering crucible. After washing, dry the precipitate as much as possible by suction, place the crucible within a larger porcelain or platinum crucible, heat gently, cool, and weigh.

The above method gives excellent results, which as a rule agree closely with those obtained by the preceding method. If the pyrite, however, contained barium or any considerable amount of lead, some sulfate will always remain undissolved with the gangue. In such cases the Lunge method will give lower results but on the other hand it represents more nearly the quantity of sulfur in the pyrite which is available for the manufacture of sulfuric acid. In spite of the strong oxidizing power of the above mixture of nitric and hydrochloric acids, it is not sufficient to permit the determination of sulfur in roasted pyrite, on account of the danger of losing some sulfur as hydrogen sulfide. Such products should be fused with sodium carbonate and peroxide as previously described.

In carrying out the Lunge method, often a little sulfur separates in dissolving the sample. It has been recommended that this sulfur be dissolved by adding potassium chlorate, but when this is done the results are likely to be high. To overcome this difficulty, Allen and Bishop recommend dissolving the pyrite in a mixture of bromine and carbon tetrachloride. The latter dissolves any sulfur that is liberated, and the dissolved sulfur is easy to oxidize.

Determination of Zinc by Potassium Ferrocyanide[1]

The potassium ferrocyanide method for titrating zinc is very accurate but it requires some experience before an operator becomes skilled in its use. The end point of the reaction corresponds to the formation of $K_2Zn_3[Fe(CN)_6]_2$.

$$3ZnCl_2 + 2K_4Fe(CN)_6 = 6KCl + \mathbf{K_2Zn_3[Fe(CN)_6]_2}$$

After this point is reached, a slight excess of ferrocyanide will give a brown coloration when tested with dilute uranyl solution or ammonium molybdate on a spot plate. If the solution contains a very small quantity of iron, a little prussian blue is formed and the color changes from pale blue to pea green at the end point as a result of the presence of yellow ferrocyanide.

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[1] The directions here given are based upon the procedure followed in the laboratories of the New Jersey Zinc Company at Palmerton, Pa.

Potassium Ferrocyanide Solution. Dissolve 32.31 g of pure ferrocyanide in water and dilute to 1 l; 1 ml of this solution should react with 7.5 mg of zinc.

Standardization. Weigh out into 400-ml beakers several 0.3-g portions of pure zinc, weighing to 4 decimal places. Cover with water and dissolve in 20 ml of 6 *N* hydrochloric acid. When all the zinc has dissolved, neutralize with strong ammonia, make slightly acid with hydrochloric acid, and add 6 ml of 6 *N* acid in excess. Add 2 drops of ferrous sulfate solution containing 2.5 g $FeSO_4 \cdot 7H_2O$ per liter. This corresponds to about 0.03 mg of iron. Dilute with water to 200 ml, heat to boiling, and titrate as follows: Reserve one-quarter of the solution in a small beaker, to avoid the necessity of titrating to the right end point at once. To the hot solution add the ferrocyanide with vigorous stirring. The solution assumes a blue color, which should be quite pale and is due to the reaction of ferrocyanide with a very small quantity of ferric iron formed from the ferrous solution added. When an excess of yellow ferrocyanide is present, the blue color changes to a pale green. Add a little more of the ferrocyanide and pour in all but about 5 ml of the reserved zinc solution. Again add ferrocyanide till the end point is reached and about 0.5 ml more. Add the last of the reserved solution, wash out the beaker with hot water, and titrate with ferrocyanide dropwise until the blue color fades sharply to a pea green. This is the end point.

Repeat the standardization until an agreement within 2 parts in 1000 is obtained.

Analysis of the Ore. Weight out into a small beaker enough of the powdered ore to give approximately 0.6 g of zinc. Moisten with water and add 10 ml of concentrated hydrochloric acid. If sulfides are present it may be necessary to add 10 ml of concentrated nitric acid at this point. Digest on the hot plate at a temperature below the boiling point for 1 hour. Remove from the plate and wash down the sides of the beaker and the cover glass. Add 10 ml of 18 *N* sulfuric acid and evaporate to fumes. With very silicious material it is well to break up the silica with a glass rod before adding the sulfuric acid. Cool and dilute to 50 ml with water.

If there is any indication of undecomposed mineral in the residue filter and wash the residue with hot water. Digest the residue with hot ammonium acetate solution to remove lead sulfate and treat the residue with sulfuric and hydrofluoric acids (cf. silicate analysis). Then, after the removal of the excess acid, fuse with potassium pyrosulfate, dissolve the melt in dilute sulfuric acid, and add the solution to that previously obtained.

The next step is to reduce the ferric salt and precipitate copper, bismuth, etc., by treatment with 1 g of 20-mesh aluminum powder at a volume of about 50 ml. If it was not necessary to test the residue for zinc, the treatment should precede the filtering of the lead sulfate and silica precipitate. Add 10 drops of saturated sodium thiosulfate solution, cover the beaker with a watch glass, and heat 20 minutes. This serves to reduce the iron and precipitate all the copper-group metals except about 0.05 per cent of cadmium, which does no harm. Transfer the solution to a 200-ml measuring flask. Make up to the mark, mix, and filter through a dry paper. Reject the first 10 ml of runnings and take 100 ml for the titration. Transfer the solution to a tall, 400-ml beaker, and neutralize with sodium hydroxide solution till a jelly is formed (of $Al(OH)_3$) and the acidity corresponds to about 2 drops of 20 per cent sulfuric acid. Use methyl orange as indicator. Add 3 ml of 5 per cent sulfuric acid, dilute to 200 ml, and introduce a stream of hydrogen sulfide into the cold solution for 40 minutes, at the rate of at least 8 bubbles per second. Allow the precipitate to settle for 15 minutes, filter, and wash with cold water.

Wash back the zinc sulfide precipitate into the beaker and rinse out the hydrogen sulfide tubing with 10 ml of concentrated hydrochloric in hot water. Run the acid through the filter and wash with hot water. Heat the acid until all the zinc sulfide has dissolved and all the hydrogen sulfide is expelled. Dilute with cold water to 150 ml, add concentrated ammonia until slightly alkaline, neutralize with hydrochloric acid, and continue as in the standardization of the ferrocyanide solution.

DETERMINATION OF ARSENIC IN ORES

Modified Method of Low-Pearce-Bennett

Of the finely powdered ore, take 0.5 g if the arsenic content is not above 10 per cent. If the ore is richer, take only enough to furnish 0.05–0.10 g of arsenic. Mix the ore with 2 g of anhydrous sodium carbonate and 1.5 g of potassium nitrate in a 30-ml porcelain crucible, and sprinkle about 1 g of the fusion mixture on top. Cover the crucible and heat very slowly over a small flame, gradually raising the temperature until finally the full heat of a good burner is used for 10 minutes. Cool and extract with 200 ml of hot water. Filter and wash with hot water until all the soluble alkali salts are removed as shown by the litmus test for sodium carbonate. In this way all the arsenic is obtained as alkali arsenate.

Make the solution distinctly acid with acetic acid and boil 10 minutes to remove carbonate and nitrite. Cool and add sodium hydroxide until the solution is basic to phenolphthalein. Discharge the color with a few drops of acetic acid and add 20 ml of 0.1 *N* silver nitrate solution. After the reddish brown precipitate of silver arsenate has coagulated sufficiently, filter and wash with cold water till the washings are free from silver. Dissolve the silver arsenate by pouring small portions of hot 3 *N* nitric acid through the filter, using about 10 ml of acid in all. Dilute and titrate the silver by the Volhard method, p. 147. One milliliter of 0.1 *N* KCNS solution = 0.002499 g of As.

Remark. This method gives excellent results in the commercial analysis of arsenide ores, but chromium and phosphorus interfere as silver chromate and phosphate, etc., behave like the arsenate.

DETERMINATION OF TITANIUM

Titanium occurs very commonly in rocks but usually only in small quantities. It occurs together with zirconium, cerium, and thorium and is very similar to zirconium in its chemical behavior.

For the determination of small quantities of titanium the colorimetric method is very satisfactory except when large quantities of iron, phosphorus, alkali salts, or even traces of vanadium are present. When these elements interfere it is not advisable to try the colorimetric determination until after they have been removed.

When titanium is unaccompanied by other cations of this group it is best to precipitate it with ammonia. The precipitate of $Ti(OH)_4$, or hydrated TiO_2, is not dissolved by an excess of ammonia and is easily converted into TiO_2 by ignition.

Usually it is necessary to remove titanium from interfering elements, and then, after the separation has been accomplished, it is best to determine the titanium volumetrically or colorimetrically.

Titanium is precipitated as hydroxide by boiling the dilute solution of the sulfate. Formerly, it was the common custom to precipitate titanium in this way, but it required such long boiling of the nearly neutral solution that it has been generally abandoned. The Gooch method depends upon adding alkali acetate and carrying out a basic acetate precipitation. The titanium precipitates in the presence of sufficient acetic acid to keep most of the aluminum in solution. The Baskerville method is based upon the fact that a nearly neutral solution of titanium and iron chlorides when boiled with sulfurous acid at moderate dilution gives a precipitate of titanium hydroxide while the iron remains in solution in the ferrous state.

The method of Barneby and Isham[1] is based on the volatilization of the silica by hydrofluoric acid in the presence of sulfuric acid, evaporation to dryness, and fusion with sodium carbonate and a little potassium nitrate (which converts the iron and titanium to insoluble ferric oxide and sodium titanate), extraction with hot water to remove the soluble phosphates, sulfates, and aluminates, solution of the ferric oxide and sodium titanate in hydrochloric acid, extraction of ferric chloride with ether, reduction of slight traces of iron with sulfurous acid, precipitation of the titanic acid by boiling in acetic acid solution, filtration, and ignition to titanium oxide (or the titanium may be determined colorimetrically). The method is accurate except that it fails to take into consideration the probable presence of zirconium and other rare earths which will precipitate with the titanium more or less completely.

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[1] *J. Am. Chem. Soc.*, **32**, 957 (1910).

Procedure. Weigh out about 0.5 g of ore into a platinum crucible, moisten with a little water, and add 5 to 10 drops of concentrated sulfuric acid and about 2 ml of hydrofluoric acid. Heat the mixture carefully until finally no more sulfuric acid fumes are evolved. Add 5–10 g of sodium carbonate and a *little* potassium nitrate,[1] and fuse the mixture at least 30 minutes. Cool, place the crucible and cover in a beaker, add about 25 ml of hot water, and heat until the melt is disintegrated. Ferric oxide and sodium titanate are left insoluble in hot water. Remove the crucible, and dissolve any adhering particles of ferric oxide and hydrolyzed sodium titanate in hot 6 *N* hydrochloric acid; save this solution. Filter off the residue in the beaker and wash with hot water.[2] Perforate the filter and carefully wash the residue into a clean beaker with 6 *N* hydrochloric acid. (No water is to be added from this stage of the analysis until after the subsequent treatment with ether.) Transfer the hydrochloric acid washings from the platinum crucible to the beaker and then heat on the hot plate until complete solution has been effected and the total volume has been reduced to 15 or 20 ml. Cool, add 2 ml of 12 *N* hydrochloric acid, and transfer the solution to a separatory funnel, rinsing the beaker with 6 *N* hydrochloric acid, *d* 1.10. Add an equal volume of ether, which has been saturated with concentrated hydrochloric acid solution, to the solution in the funnel, insert a rubber stopper in the top, invert the funnel, open the stopcock, and shake thoroughly. Close the stopcock, place the separatory funnel in an upright position, and allow to stand 10 minutes. Then drain off the aqueous layer into a second separatory funnel. Rinse the ether twice by shaking well with 5- to 10-ml portions of 6 *N* hydrochloric acid, and add the washings to the aqueous solution. Repeat the treatment with ether two or three times until the last portion of ether fails to show any greenish tinge due to the presence of dissolved ferric chloride.

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[1] The potassium nitrate is added to make sure that the crucible is not injured by any sulfide or reducible metal which may be present. Too much nitrate should not be added; it will injure the crucible and also cause the melt to effervesce badly.

[2] The residue should not be washed with too much hot water; the hydrolysis of the sodium titanate may go so far that the residue will not dissolve in hydrochloric acid.

Rothe,[1] who first made use in quantitative analysis of the fact that ferric chloride dissolved in hydrochloric acid, *d* 1.1, can be removed by shaking with ether, recommended the double separatory funnel shown in Fig. 45, but an ordinary 125-ml single separatory funnel can be used satisfactorily.

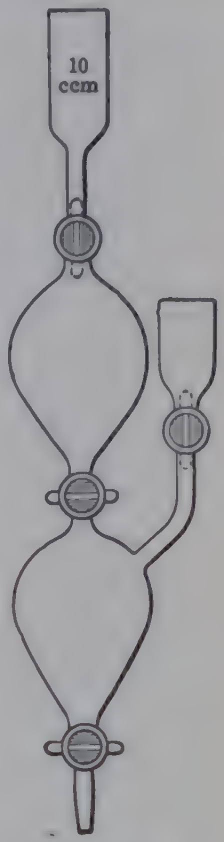

FIG. 45.

Carefully heat the aqueous solution containing all the titanium in the presence of little, if any, iron and aluminum, on a water bath containing warm water to expel the dissolved ether, add 20 ml of 18 *N* sulfuric acid, and evaporate the solution until fumes of sulfuric anhydride are evolved. Dilute the cooled solution to about 100 ml and nearly neutralize with ammonia. Add 1–2 g of ammonium bisulfite and heat the solution on the hot plate for half an hour. Now add 10–15 g of ammonium acetate, with 5–10 ml of glacial acetic acid, and boil the solution for 15 minutes. Filter, wash with 7 per cent acetic acid, ignite, and weigh as TiO_2.

Rapid Volumetric Method

The following procedure has proved useful for the rapid evaluation of ores and titanium products.

Weigh out about 0.5 of the finely powdered sample into a dry, heavy-walled, 8-in. test tube and mix it with about 7 g of powdered $K_2S_2O_7$ (made by fusing $KHSO_4$ to a quiet melt from which SO_3 is beginning to escape, pouring out upon a tile and powdering). Tap the sides of the tube to drive down adhering particles, and clamp the tube in a vertical position but fixed so that later it can be swung to a nearly horizontal position. Heat the mass gently until the flux has melted and all water has expelled. When an orange coloration is seen at the sides of the tube near the surface of the melt, raise the temperature gradually to redness and continue fusing until there are no more bubbles rising from the bottom and the solid particles of ore have all disappeared. Then heat any portion of the tube where there is evidence of spattering. By changing the position of the clamp, raise the bottom of the tube and allow the melt to flow halfway up the sides of the tube; clamp the tube in this nearly horizontal position. In a few minutes the mass will solidify and the melt will usually crack so that it can be dislodged from the tube with the aid of a steel spatula.

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[1] *Z. anal. Chem.*, **1901**, 809.

Add to the tube 30 ml of 18 N H_2SO_4 and heat until the melt has dissolved to a clear solution, in which the titanium is present as $Ti(SO_4)_2$. Disregard a slight turbidity which may be silica or a difficultly soluble sulfate. If any TiO_2 forms by hydrolysis, it can usually be distinguished by its relatively high index of refraction and appears as sharply contrasted white clots. These can usually be dissolved by adding 2 ml of concentrated H_2SO_4 and boiling gently. Sometimes it is necessary to discard the sample.

Dilute the solution to about 250 ml and pass through a Jones reductor as described on p. 116, but use very little suction and have a piece of marble weighing about 5 g in the flask to provide an atmosphere of CO_2, but with no ferric sulfate solution in the flask. First pass 50 ml of 3–5 per cent H_2SO_4 through the cleaned and tested reductor containing amalgamated zinc (cf. p. 114), then the titanium solution, then 100 ml more of 3–5 per cent acid, and finally 100 ml of water. Remove from the reductor, add 5 ml of 20 per cent KCNS solution, and titrate with standard ferric alum solution until noticeable red color of $Fe(CNS)_3$ is permanent for 90 seconds. Run a blank to determine how much of the ferric alum solution is necessary to give an end point with 500 ml of 3 per cent H_2SO_4 and 5 ml of the indicator. To prepare the ferric alum solution, dissolve 50 g of $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ in 1 l of 0.5 N H_2SO_4, and standardize by the above procedure against 0.2-g portions of pure TiO_2.

$$Ti^{+++} + Fe^{+++} \rightarrow Ti^{++++} + Fe^{++}$$
$$Fe^{++} + 3CNS^{-} \rightarrow Fe(CNS)_3 \quad \text{red end point}$$

DETERMINATION OF TUNGSTEN IN ORES[1]

Procedure. Weigh out accurately about 1 g of the finely ground ore into a 400-ml beaker. Moisten the sample with 5 ml of water, and add 100 ml of concentrated hydrochloric acid. Cover the beaker and digest at about 60° for at least an hour. Stir from time to time to prevent the formation of any crust. Then evaporate slowly to about 50 ml. Add 40 ml more of strong hydrochloric acid and 20 ml of concentrated nitric acid, and evaporate to about 10 ml. During these operations, especially when fresh acid is added, stir the material at the bottom of the beaker so that it does not become encrusted.

Rinse down the cover glass and the sides of the beaker and dilute with water to about 150 ml. If, by accident, the solution was evaporated to dryness during the above treatment, add 20 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid to the residue and evaporate to 10 or 15 ml.

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[1] Recommended by J. A. Holliday and found satisfactory by collaborative work in 17 different laboratories under the direction of W. F. Hillebrand.

To the diluted solution add 5 ml of cinchonine hydrochloride solution (12.5 g of cinchonine dissolved in 100 ml of 6 *N* hydrochloric acid) and heat on the hot plate for 30 minutes or longer. The solution should be at a temperature just below the boiling point and should be stirred occasionally.

Allow the tungstic acid anhydride to settle and then decant the solution through a filter which contains some pulp made by digesting ashless filter paper with acid. Wash the precipitate three times with a solution containing 10 ml of the above cinchonine solution to a liter of hot water. Then transfer the precipitate to the filter and wash with this same, diluted cinchonine solution.

Wash the tungstic anhydride back into the original beaker by a jet of water, using about 25 ml to accomplish this. Add 6 ml of concentrated ammonia solution and heat gently, with the beaker covered, for about 10 minutes to convert all the tungstic acid into ammonium tungstate. Rinse down the sides of the beaker with hot, dilute ammoniacal ammonium chloride solution (200 ml of concentrated ammonia, 800 ml of water, and 10 ml of concentrated hydrochloric acid). Stir up the contents of the beaker and filter through the same filter that was used for the previous filtration. Collect the filtrate in a 400-ml beaker and wash the original beaker and filter with the hot ammoniacal solution. The presence of a little ammonium chloride in this ammoniacal solution prevents colloidal silicic acid from passing into the filtrate.

The residue on the filter is usually free from tungsten, but it should be tested (see below). Ammonium and sodium salts tend to prevent the complete precipitation of tungstic acid, so that it is important, next, to remove the excess ammonia. After this has been evaporated off, add 20 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid and evaporate to about 15 ml. Dilute with 150 ml of water and precipitate the remainder of the tungstic acid by treatment with cinchonine solution as described above.

After filtering and washing the precipitate as before, ignite it carefully in a weighed platinum crucible. The presence of the paper pulp causes the precipitate to form a porous, friable mass and makes it easy to oxidize the carbon. If the ignition is made in a muffle, the introduction of oxygen is advantageous. After burning off the carbon, at as low a temperature as possible, weigh the precipitate and correct for silica by the usual treatment with hydrofluoric acid.

If the tungstic acid is heated over the full flame of the burner, some of it will be lost by volatilization. After the removal of the silica, the residue should be heated to dull redness for only 1 minute. Heated in the muffle, the maximum temperature should not exceed 800°. The ignited tungsten trioxide, WO_3, should have a clean, lemon-yellow color.

To test for tungsten the residue that is insoluble in ammonia, ignite it in an iron crucible and fuse the ash with a small quantity of sodium peroxide mixed with a little sodium carbonate. Reducible metals are likely to ruin a platinum crucible if the residue and filter paper are heated in it. Extract the melt with water and filter. Acidify the aqueous extract with hydrochloric acid, add 5 ml of cinchonine hydrochloride solution, and heat for several hours to see if any yellow tungstic acid anhydride is formed.

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57. Compute the volume of fuming HNO_3 required to oxidize and dissolve 3.505 g of FeS_2. Assume the acid to be *d* 1.500, to contain 94.1 per cent HNO_3 by weight, and to be reduced to NO_2. Compute the weight of dry Na_2O_2 required to carry out the same oxidation if the peroxide contains 40 per cent Na_2CO_3.

58. How many cubic feet of air at 130°F and 27 in. mercury pressure would be required theoretically to burn 1 lb of pure FeS_2? What would be the volume of the gaseous residue at the same temperature and pressure? Assume Fe_3O_4 and SO_2 formed and air to contain 20 per cent oxygen.

59. What weight of pyrite should be taken so that the weight of $BaSO_4$ multiplied by 100 will give the percentage of S in the sample?

60. Compute the weight of Na_2O_2 required in the analysis of 0.5 g FeS_2. Why should an excess be used, and what happens to the excess? After the Na_2O_2 fusion how does Mn behave when the melt is treated with water?

61. What weight of pyrite should be taken so that the weight of the $BaSO_4$ precipitate multiplied by 25 gives the percentage of S present?

62. What weight of zinc ore should be taken for analysis so that the number of milliliters of 0.09 M ferrocyanide used will be the same as the percentage of Zn in the ore?

63. Two portions of a single titanium ore, each weighing 0.80 g, are taken for analysis. In one portion the iron alone is determined after careful reduction with $SnCl_2$ (stopping before any titanium is reduced) and titration by the Zimmermann-Reinhardt method (see p. 116) with 26.0 ml of $KMnO_4$ solution of which 1 ml would oxidize 0.80 ml of a potassium tetroxalate solution that was 0.08 N *as an acid.* In the other sample, the Fe^{+++} is reduced to Fe^{++} and Ti^{++++} to Ti^{+++} and then both oxidized back with 48 ml of the same $KMnO_4$ solution. Assuming that the original sample contained Fe_3O_4, TiO_2, and SiO_2 only, compute the percentage of each present.

64. What weight of titanium ore should be taken for analysis, so that the milliliters of ferric solution containing 10 g of Fe per liter required to react with Ti^{+++} shall be 4 times as great as the percentage of Ti in the ore? (In this method of analysis all the Ti^{++++} is reduced to Ti^{+++} and then titrated in an atmosphere of CO_2 with Fe^{+++} solution until a drop of the Fe^{+++} gives a red color with CNS^- which has been added. $Fe^{+++} + Ti^{+++} \rightarrow Fe^{++} + Ti^{++++}$.)

65. Compute the percentage of As in an ore when 0.45 g of the ore yielded a precipitate of Ag_3AsO_4 which after being dissolved in dilute nitric acid reacted with 23 ml of 0.08 N KCNS solution.

66. A method for determining arsenic has been proposed which depends upon the formation of AsH_3, oxidation of the AsH_3 to AsO_4^{---} by iodine solution, and titration of the excess iodine with sodium thiosulfate solution. The reactions are

$$AsH_3 + 4I_2 + 11HCO_3^- \rightarrow AsO_4^{---} + 8I^- + 11CO_2 + 7H_2O$$
$$I_2 + 2S_2O_3^{--} \rightarrow 2I^- + S_4O_6^{--}$$

If in the analysis 0.250 g of material, 50 ml of 0.125 *N* iodine solution, and 20 ml of thiosulfate (1 ml = 0.005 g Cu) are used, compute the percentage of As_2O_3 present in the sample.

67. If the same weight of sample as in Problem 66 had been analyzed by the Pearce method, how many milliliters of KCNS solution (1 ml = 0.002 g of Ag) would have been used in the final titration?

68. If in the analysis described in Problem 66, the solution of arsenite was reduced to AsH_3 electrolytically with a current of 3 amperes and current yield of 40 per cent AsH_3 and 60 per cent H_2, compute the time required for the electrolytic reduction

$$AsO_3^{---} + 6e + 9H^+ \rightarrow AsH_3 + 3H_2O$$

69. It has been proposed to determine tungsten by measuring the volume of NaOH solution required to dissolve a precipitate of WO_3 and form Na_2WO_4. If, in the analysis of 0.45 g of ore, 25 ml of 0.15 *N* NaOH was used to dissolve the WO_3 and the excess of alkali hydroxide reacted with 12 ml of 0.18 *N* HCl, find the percentage of W present in the ore.

CHAPTER XXI

ANALYSIS OF BEARING METALS (ANTI-FRICTION METALS)

The analysis of bearing metals is one that the practical chemist is often called upon to make because these alloys are usually sold and purchased under fairly rigid specifications concerning the chemical composition. The alloys are not difficult to analyze if suitable methods are followed; otherwise the results are likely to be erratic. The National Bureau of Standards has prepared at least three different alloys of this type, and, before sending these out for chemists to use in testing their methods of analysis, each alloy has been analyzed in ten different laboratories with good agreement with respect to the various values. In making a commercial analysis, the time factor often has to be taken into consideration. If, for example, a given sum is paid for having an analysis made, the chemist ought not to spend more than a corresponding amount of time in carrying out the work. A method, therefore, which will give results that are approximately correct is often more valuable than one which will give somewhat more accurate values but only with the expenditure of considerably more time and labor. In selecting the methods to be described in this chapter, the time necessary for carrying out the work has been taken into consideration. The methods have been tested in the laboratory with students and found to give satisfactory results although some of the procedures recommended are not the best known for accurate scientific work. Duplicate values that agree well in any analysis merely mean that the operator has carried the analysis out twice in the same way, and when these values are near the truth it usually means that the sum of the positive and negative errors is equal to zero rather than that no error has been made.

There are three important classes of bearing metals: the phosphor bronzes, the lead-base alloys, and the tin-base white alloys. The alloys of copper, tin, and antimony were first recommended by Isaac Babbitt of Massachusetts for bearings in "journal boxes," and the name Babbitt's metal is now applied to almost any white anti-friction alloy.

The phosphor bronzes are essentially alloys of copper, tin, and phosphorus, but they may contain lead and traces of other elements. They are used for bearings of high-speed machinery and will stand fairly heavy loads. For bearings they possess a low coefficient of friction and are hard enough to resist abrasion. With respect to their malleable qualities a distinction is made between *malleable* phosphor bronzes and *cast* phosphor bronzes. The former contain not more than 6 per cent of tin or 0.3 per cent phosphorus. The malleability is due to the formation of a homogeneous solid solution of Cu_3P in copper with small quantities of phosphorus, and when more phosphorus is present a finely divided Cu-Cu_3P eutectic is often found. These alloys are used for wire, gear wheels, pinions, bushings, worm wheel rims, etc.

The *cast* phosphor bronzes are well suited for bearings. The upper limits for tin and phosphorus may be placed at 12 and 1.5 per cent. Sometimes as much as 10 per cent of lead is present. These alloys show under the microscope a hard crystalline constituent embedded in a softer, plastic matrix. The load is carried by the harder material, and the plastic material provides for continuous lubrication. The presence of lead increases the amount of the plastic constituent.

ANALYSIS OF PHOSPHOR BRONZE

Standard Sample 63 of the National Bureau of Standards contains, in addition to copper, tin, lead, and phosphorus, 0.55 per cent of antimony, 0.48 per cent of zinc, 0.27 per cent of iron, 0.20 per cent of arsenic, 0.05 per cent of sulfur, 0.05 per cent of aluminum, and 0.008 per cent of nickel. In the procedure to be described only the first four elements will be considered. In this procedure, the antimony will be determined with the tin in a precipitate of " metastannic acid " and will be counted as tin. The arsenic will also be present in this precipitate as As_2O_5.

Determination of Copper and Lead

Procedure. Dissolve 0.5 g of borings in a small beaker with 15 ml of 6 N nitric acid, d 1.2. Evaporate the solution just to dryness on the water bath, and remove the beaker as soon as this stage is reached. Treat the residue with 20 ml of 2 N nitric acid, heat to boiling, and decant off the solution through a hardened filter paper. Repeat this treatment. Complete the washing by boiling and decanting with 1 per cent ammonium nitrate solution. Keep as much of the precipitate as possible in the original beaker, and the total volume of the filtrate under 150 ml. Examine the first portions of the filtrate for metastannic acid, refilter if necessary, and remove each successive portion from below the funnel before adding more wash water. Wash the precipitate with 1 per cent NH_4NO_3 solution until a portion of the filtrate will give no test for copper or lead on adding a little ammonium sulfide solution (or for copper with $K_4Fe(CN)_6$ solution). Save the precipitate for the tin determination.

To determine the copper and lead electrolyze this solution, and the nitric acid solution obtained below, with platinum gauze electrodes; use a current of 0.25 ampere for 4 to 6 hours and then one of 0.1 ampere for 18 to 20 hours. The copper will be deposited on the cathode as metallic copper and the lead upon the anode as PbO_2. (See p. 231.)

Determination of Tin

With the aid of a stream of water from a wash bottle, transfer the insoluble residue back to the original beaker as completely as possible, but limit the quantity of water used as far as practicable. To dissolve the precipitate remaining on the filter, spread it out on the bottom of a beaker, pour over it 25 ml of yellow ammonium sulfide solution, and heat gently for 15 minutes. Meanwhile add 75 ml of the sulfide solution to the residue in the original beaker. Add to this the ammonium sulfide solution from the treatment of the filter paper, and wash the paper 3 times with hot water. Save the filter paper.

Cover the beaker containing the ammonium sulfide solution with a watch glass and digest at 60° to 70° for 2 hours. Then filter off any black residue and collect the filtrate in a 600-ml beaker. Wash the residue with 100 ml of ammonium sulfide reagent which has been diluted with 4 times as much water. Complete the washing with water. Treat this filter and the one previously saved with 15 ml of hot 3 N HNO_3, filter, wash free from acid with hot water, and add this solution, after nearly neutralizing it with ammonia, to that in which the copper and lead is to be determined (see above). Add the residue to the Sn precipitate.

To the ammonium sulfide solution add acetic acid until the solution reacts acid, and allow to stand in a warm place for at least 3 hours. Then filter off the SnS_2 precipitate and wash it with 2 per cent NH_4NO_3 solution, using at least 150 ml of it. Transfer the moist SnS_2 precipitate to a weighed porcelain crucible and ignite carefully. Call the residue SnO_2, and report the percentage of tin present in the alloy.

Determination of Phosphorus[1]

Weigh out 1–3 g of sample into a 300-ml Erlenmeyer flask and dissolve in 20 ml of aqua regia. When all the metal has dissolved add 10 ml of water and digest at 90° for 10 minutes. Dilute to 50 ml and treat with 100 ml of ammonium molybdate solution prepared as recommended by Blair (see p. 249).

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[1] Method of Lundell and Hoffman, *Ind. Eng. Chem.* **15**, 172 (1923).

Stopper the flask with a rubber stopper and shake for 10 minutes, occasionally removing the stopper. Allow to stand 4 hours or longer before filtering. Filter, keeping as much as possible of the precipitate in the flask. Wash the precipitate 5 times by decantation with 10-ml portions of 1 per cent nitric acid.

Dissolve the precipitate on the filter in 5 *N* ammonium hydroxide containing 0.5 g of citric acid. Pour this on the filter in small portions, and catch the filtrate in the original flask containing the bulk of the precipitate. Do not use more than 50 ml of the ammonium hydroxide. Warm the solution slightly to dissolve the precipitate, replace under the funnel, and wash the filter with a little hot 5 per cent hydrochloric acid. If the ammoniacal filtrate is not clear at this stage, filter through the same filter and wash the filter with hot water.

Make the solution acid with hydrochloric acid, and, without regard to a slight precipitate of molybdic acid, which, however, seldom forms in the analysis of alloys with low phosphorus, add 20 ml of magnesia mixture (p. 205). Heat to boiling and slowly add ammonium hydroxide till a precipitate forms or the solution is ammoniacal. Finally add enough 15 *N* ammonium hydroxide to make the solution 1.5 *N* with ammonia and allow to stand 4 hours. Filter, wash with cold 1.5 *N* ammonium hydroxide, and finish the analysis as described on pp. 205 and 206.

ANALYSIS OF BABBITT'S METAL

The National Bureau of Standards distributes two standard alloys: one containing about 79 per cent lead, 11 per cent tin, and 10 per cent antimony; and another containing about 88.3 per cent tin, 7.3 per cent antimony, 3.8 per cent copper, and 0.6 per cent lead. The alloys contain traces of iron, bismuth, and arsenic which need not concern us here.

Determination of Lead

Take samples of about 0.4 g, weighed carefully to four significant figures. Treat each sample in a 250-ml Erlenmeyer flask with 25 ml of a saturated solution of bromine in concentrated hydrochloric acid. After a few minutes, heat gently but take care not to boil off all the bromine until the alloy is entirely decomposed. Pay no attention to the formation of a white precipitate of lead chloride. When none of the original alloy remains, heat to expel the excess bromine; the solution will become colorless or pale yellow in color. Remove from the heat and cool somewhat. Add 15 ml of 18 N H_2SO_4 (concentrated acid added carefully to an equal volume of water) and evaporate until dense fumes of sulfuric acid are evolved and all HCl is expelled. Cool, dilute to about 100 ml, and allow to stand at least an hour. Filter through a Gooch crucible that has been washed with alcohol and with ether and weighed after heating to about 400° (see p. 192). Wash the precipitate under gentle suction with six 5-ml portions of 1.8 N H_2SO_4 and then with six portions of alcohol and finally four portions of ether. Dry the crucible at 105° for about 15 minutes, and then heat strongly inside a large crucible; cool in a desiccator and weigh. Report the percentage of lead in the alloy.

Sometimes the results are high because some undissolved alloy remains with the lead sulfate. To recover this, wash the weighed $PbSO_4$ repeatedly with hot 2 N $NH_4C_2H_3O_2$ until the washings give no test with K_2CrO_4 solution; heat as before, cool, and weigh. Deduct the weight of residue from that of the impure precipitate and make a corresponding correction in the antimony determination.

Determination of Antimony

Digest accurately weighed 0.4-g samples of alloy in 250-ml flasks with 12 ml of concentrated H_2SO_4 and about 5 g of $KHSO_4$. Heat over a free flame while constantly rotating the contents of the flask until all the metal has dissolved and the contents of the flask fume strongly.

It is desired to get the antimony into solution as $Sb_2(SO_4)_3$ and the tin as $Sn(SO_4)_2$.

$$2Sb + 6H_2SO_4 = Sb_2(SO_4)_3 + 3SO_2 + 6H_2O$$
$$Sn + 4H_2SO_4 = Sn(SO_4)_2 + 2SO_2 + 4H_2O$$

If the alloy is heated too gently, sometimes a part of the tin is left in the stannous condition, and this is fatal to the analysis. The acid should be heated nearly to the boiling point to accomplish the second stage in the oxidation of the tin. A black residue of finely divided antimony often requires prolonged heating.

When the sample is completely decomposed and the sulfuric acid has fumed strongly for several minutes, allow to cool and then add very cautiously 5 ml of water. Follow this with 20 ml of 12 N hydrochloric acid and boil gently for 3 minutes. Cool, add 100 ml of cold water, and titrate at a temperature below 15° with 0.1 N permanganate. The end point should remain for 20 seconds if the above directions were followed. Save the solution for the tin determination.

According to Lundell,[1] the solution should contain 10 to 25 per cent of concentrated HCl by volume, and approximately 10 per cent by volume of concentrated H_2SO_4 is desirable. The above directions provide for 10 per cent of HCl and somewhat less than 6 per cent of H_2SO_4 by volume. The procedures recommended by the

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[1] *Applied Inorganic Analysis*, p. 228.

Bureau of Standards and by Lundell, Hoffman, and Bright call for less than 5 per cent H_2SO_4. The titration of antimony with permanganate gives very accurate results when the conditions are right, and this method of determining antimony is used more than any other in commercial testing. If the conditions are not right, the end point may be very hard to find. For many years chemists avoided as much as possible all titrations with permanganate in the presence of hydrochloric acid because hydrochloric acid is easily oxidized to chlorine or hypochlorous acid, a reaction which is catalyzed by the presence of other substances such as ferrous salt. By keeping the solution cold, by making sure that all tin, iron, etc., is oxidized by sufficiently long treatment with hot sulfuric acid, and by adding appropriate quantities of hydrochloric and sulfuric acids, this oxidation of HCl is prevented. The titration reaction can be expressed as follows:

$$5Sb^{+++} + 2MnO_4^- + 12H_2O = 5H_3SbO_4 + 2Mn^{++} + 9H^+$$

and the milliequivalent of antimony is 0.06088 g.

Determination of Tin

Transfer the titrated solution from the antimony determination to a 500-ml Erlenmeyer flask; add 65 ml more of concentrated hydrochloric acid and about 2 g of test lead powder. Stopper the flask with a rubber stopper carrying a long glass tube which extends from the bottom of the stopper upward for about an inch and then bends downward through a wide arc to a point on the outside nearly level with the bottom of the flask when the stopper is inserted. Heat the contents of the flask to boiling and boil gently for 30 minutes. Then remove the flame and, without removing the stopper from the flask, insert the outer end of the tubing it carries into a beaker containing 200 ml of saturated $NaHCO_3$ solution (about 22 g of $NaHCO_3$). While keeping the tubing in this $NaHCO_3$ solution, cool the contents of the flask by cold, running water. Cool slowly at first. At the end of the reduction with lead,

$$Sn^{++++} + Pb = Sn^{++} + Pb^{++}$$

the flask is filled with steam; but as the contents cool and the steam condenses, the $NaHCO_3$ solution is sucked into the flask and CO_2 is formed which exerts a pressure and will force back the liquid in the tubing and perhaps bubble through the $NaHCO_3$ solution. In this way the flask becomes filled with CO_2 rather than air, of which the oxygen would oxidize some of the stannous ions back to the stannic state. Finally cool to about 10° (using ice-water or Dry Ice if necessary), add 5 ml of starch indicator solution, and titrate fairly rapidly with 0.1 *N* iodine solution.

$$Sn^{++} + I_2 = Sn^{++++} + 2I^-$$

Instead of using the above device for filling the flask with CO_2, a stream of CO_2 gas can be kept passing through the solution during the reduction with Pb and particularly during the cooling of the solution. Some chemists add a lump or two of calcite ($CaCO_3$) to the reduced solution which slowly dissolves in the acid with liberation of CO_2. A little Dry Ice placed in another flask will furnish a convenient source of CO_2. On placing this flask in warm water, an abundant stream of CO_2 is evolved which can be led into the flask containing the solution of the alloy by means of tubing extending nearly to the bottom of the flask containing the solution that is being analyzed. The above scheme of sucking $NaHCO_3$ back into the solution works nearly as well. It has been recommended that the iodine solution be added through tubing that runs through the stopper so that there is absolutely no chance for air to enter the flask during the titration. The titration of $SnCl_2$ with iodine is very accurate, but it is necessary to have all the tin in the stannous condition and to prevent any back oxidation by air, or the results of the analysis will be low. Various other reducing agents such as a coil of nickel wire, metallic iron, or powdered antimony have been recommended instead of the test lead, but in every case the chief source of trouble is oxidation by the air.

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70. From 0.400 g of alloy there was obtained 0.260 g of $PbSO_4$. (*a*) If this were dissolved in ammonium acetate and the solution treated with potassium chromate solution under ideal conditions, how much $PbCrO_4$ would be obtained? (*b*) If the lead chromate precipitate were analyzed iodimetrically, how many milliliters of $Na_2S_2O_3$ solution (1 ml = 0.0084 g Cu) would be required to liberate the I_2 formed by treating the chromate precipitate with acid and excess KI? (*c*) What percentage of Pb was present in the alloy?

71. What is the minimum time required for electrolysis in the analysis of a brass containing 64 per cent Cu and 1.56 per cent Pb?

72. In the analysis of 2.05 g of an alloy, there was obtained 0.0046 g of $Mg_2P_2O_7$. (*a*) Find the percentage of P in the alloy. (*b*) If the $MgNH_4PO_4 \cdot 6H_2O$ had been weighed after washing with alcohol and ether (see p. 205), what would have been the weight? (*c*) If the phosphorus had been determined (as is often done) by the alkalimetric method used in the analysis of steel (see p. 252), how many milliliters of 0.25 *N* HNO_3 would have been required to titrate the excess of NaOH when 25 ml of 0.22 *N* NaOH were used to dissolve the yellow phosphomolybdate precipitate?

73. Find the percentage of antimony present in an alloy from the following data: weight of sample = 0.450 g; used 12.2 ml of $KMnO_4$ solution; 1 ml $KMnO_4$ = 0.0065 g Fe.

74. Find the percentage of tin in an alloy from the following data: weight of alloy = 0.420 g; used 18.6 ml of I_2 solution of which 1 ml = 0.0056 g As_2O_3.

75. Arsenic in an alloy is sometimes determined by distilling it off as $AsCl_3$ together with HCl, neutralizing the distillate and titrating with iodine in the presence of $NaHCO_3$ and starch. Compute the percentage arsenic in an alloy from the following data: weight of alloy 6.00 g; used 16.4 ml of iodine solution of which 1 ml = 0.0024 g Sb.

76. Sometimes arsenic is determined by forming AsH_3 and absorbing it in a measured volume of iodine solution. Eventually the absorbed AsH_3 is oxidized to arsenate by the iodine and the excess is titrated with $Na_2S_2O_3$ solution. If the alloy mentioned in Problem 75 were analyzed in this way, and with the same weight of sample, how many milliliters of 0.08 *N* iodine would be required for the absorption and oxidation of the AsH_3?

CHAPTER XXII

POTENTIOMETRIC TITRATIONS

In other parts of this book, particularly in Chapters V and XIII, it was shown that the oxidation potential of any equation of oxidation-reduction depends upon the concentration of every ion in solution that takes part in the reaction. If a metal is in contact with a solution of its ions and the reaction studied is

$$M - ne = M^{n+}$$

the Nernst formula shows that

$$E_{30^\circ} = E_0 + \frac{0.060}{n} \log c$$

in which E_{30° is the actual potential which prevails at 30°, E_0 is the *normal* oxidation potential, which can be obtained from the table of oxidation potentials and refers to a *molar* solution of the ions, n is the change in valence, and c is the concentration of the ions in moles per liter. The relation between a hydrogen electrode and a solution of its ions can be regarded in the same way. To be sure, the solubility of hydrogen gas is greater than that of most metals, but the saturated solution at 30° is only 0.00076 M and, moreover, the hydrogen electrode is kept saturated with hydrogen gas, so that it is not necessary to take the concentration of dissolved hydrogen gas into consideration. The normal oxidation potential of hydrogen is arbitrarily taken as 0.00 and the valence change is 1, so that the above equation becomes for hydrogen

$$E_{30^\circ} = 0.060 \log c$$

and since $-\log c$ for hydrogen ions is the $p\text{H}(= \log 1/[\text{H}^+])$ we have

$$E_{30^\circ} = -0.060\ p\text{H} \quad \text{or} \quad p\text{H} = -E_{30^\circ} \div 0.060$$

If, therefore, we measure the potential between a hydrogen electrode and a solution of its ions, it is easy to calculate the pH of the solution.

If a hydrogen electrode (a small piece of platinum foil covered with platinum black and kept saturated with hydrogen gas) is placed in a solution together with an electrode of known electromotive force such as a calomel electrode, and the electrodes are connected externally, a current will flow if there is any difference in potential between the hydrogen electrode and the standard electrode. The voltage can be measured by sending a current from a dry cell in the opposite direction and measuring the voltage of this second current when it just suffices to neutralize the original current.

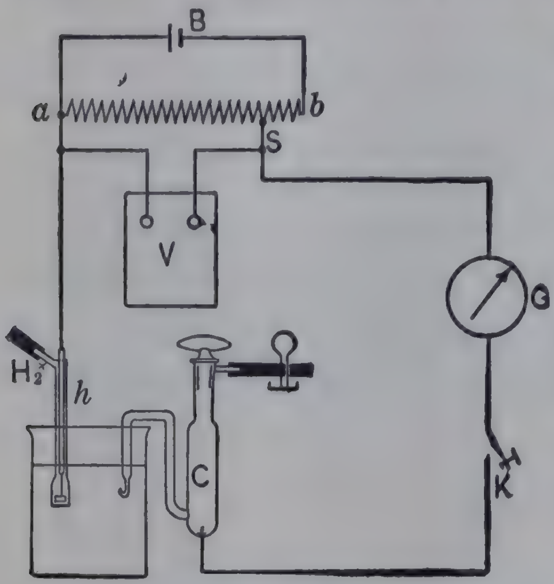

FIG. 46.

Figure 46 is a diagram of such an arrangement as used by Hildebrand.[1] A beaker contains the hydrogen electrode *h*, the solution to be tested, and the calomel electrode *C*; the last is connected through the switch *K* with the galvanometer *G* and thence to the positive pole of the dry cell *B*. By means of the sliding contact *S*, a variable fraction of the current can be made to pass from the dry cell through a galvanometer to the calomel electrode, opposing the current which results from the potential difference between the two electrodes in the solution. When the two emf's are equal, no current flows in the wire, as shown by the needle of the galvanometer, and the voltage can be read at *V*.

In any aqueous solution at 30° the equation [concn. H^+] × [concn. OH^-] $= 10^{-14}$ holds, when the concentrations are expressed in moles per liter. If, therefore, the concentration of the hydrogen ion is established by measurement, the concentration of the hydroxyl ion is also known and the alkalinity as well as acidity of any solution can be expressed by simply stating the hydrogen-ion concentration of the solution.

If log 1/OH is called pOH then $p\text{H} + p\text{OH} = 14$ in all cases.

The method of measuring electromotive force by Poggendorff's compensation method was outlined on p. 226 with a set-up like that of Fig. 46. By combining the slide-wire bridge $a-b$ and the voltmeter *V* as in the Laboratory Hydrogen Ion Potentiometer of the Leeds & Northrup Company shown in Fig. 47, the voltage can be measured with an accuracy of about 0.03 per cent. With a suitable galvanometer and with solutions having a resistance of not over 100,000 ohms, measurements can be made to 0.05 millivolt, which corresponds to 0.01 pH unit.

The use of the potentiometer will not be described in further detail here because full directions are furnished by the makers of the apparatus. In Fig. 47, the beaker on the right contains the hydrogen electrode and the solution to be tested; above it are two burets containing acid and base, respectively. The beaker on the left contains potassium chloride of suitable concentration. This makes what is called a *salt bridge*; it provides electrical contact between the calomel electrode on the left and the hydrogen electrode on the right. The electrical connection between the wire at the bottom of the calomel cell should be with the binding post marked + on the potentiometer and the hydrogen electrode should be connected with the binding post marked −. It is convenient to provide a mechanical stirrer, if a titration is to be made with this set-up. It is best to stop stirring while a reading is being taken. In working with the above set-up, the commonest error is to connect the electrodes wrongly; the chief inconveniences are the maintenance of a steady stream of purified hydrogen gas and the care of the platinum black electrode, which sometimes becomes *poisoned*, especially when the solution contains ammonia or hydrogen sulfide.

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[1] *J. Am. Chem. Soc.*, **35**, 847 (1913).

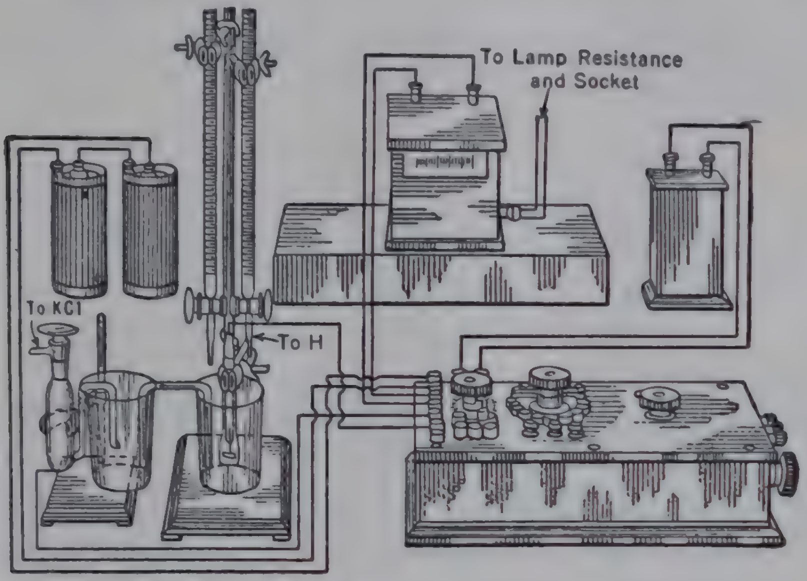

FIG. 47.

Besides the above instrument, which can be made to give direct pH readings, various other models are now on the market. Instead of the two dry cells shown in Fig. 47, two Edison cells or a lead accumulator cell is better.

Every potentiometric determination requires the use of two electrodes of which one is dipped into the solution tested and the other into a standard solution. These electrodes are called respectively the *indicator electrode* and the *reference electrode*. In the above set-up, the hydrogen electrode was the indicator electrode and the calomel cell the reference electrode. The single potential of the calomel cell varies with the temperature and with the concentration of the potassium chloride solution; three concentrations are commonly used, *normal*, *tenth-normal*, and *saturated* (cf. p. 227).

Quinhydrone Electrode. Another indicator electrode which is much used in determining *p*H values below 7 is the so-called *quinhydrone electrode.* It consists of a *bright* platinum or gold foil which is placed in the solution to be tested, and to each 100 ml of the solution is added about 1.1 g of quinhydrone. With the quinhydrone electrode, the solution can be stirred vigorously while the readings are being taken, the work is much less tedious than when a hydrogen electrode is used, and a suitable titration outfit is much less expensive. Quinhydrone is a molecular compound containing equimolecular proportions of quinone, $C_6H_4O_2$, and hydroquinone, $C_6H_4(OH)_2$.

Quinone can be reduced electrolytically in acid solution with the formation of hydroquinone. The reaction is perfectly reversible and can be expressed as follows:

$$C_6H_4O_2 + 2H^+ + 2e \rightleftarrows C_6H_4(OH)_2$$

The oxidation potential of this reaction can be expressed as follows:

$$E_{30^\circ} = E_0 + \frac{0.060}{2} \log \frac{[H]^2[A]}{[H_2A]}$$

when [A] and $[H_2A]$ represent the concentrations of $C_6H_4O_2$ and $C_6H_4(OH)_2$ in moles of dissolved substance per liter. Since, however, quinhydrone is an equimolecular compound of quinone and hydroquinone, $[H_2A] = [A]$, and the log of $[H^+]^2 = 2 \times \log [H^+]$, the equation becomes

$$E_{30^\circ} = E_0 + 0.060 \log H^+$$

or

$$E_{30^\circ} = E_0 - 0.060\, p\text{H}$$

which tells us that *the potential of the quinhydrone electrode changes with the* pH *of the solution in exactly the same way that the hydrogen electrode does.*

The value of E_0 in the above equation is about +0.705 volt at 25° and that of the 0.1 *N* calomel electrode is +0.338 volt. The calomel electrode, therefore, is negative to the quinhydrone electrode until a *p*H of about 6.2 is reached, whereas the calomel electrode is always positive to the hydrogen electrode. It is sometimes stated that the quinhydrone electrode can be used only in acid solutions because in alkaline solutions the hydroquinone is oxidized to a fairly strong acid and the ratio H_2A/A is no longer equal to unity. The *p*H values, to be sure, are inaccurate in alkaline solutions (see below) but fairly good end points in a titration can be obtained as follows: At the start of a titration of an acid with a base, connect the calomel electrode to the negative binding post and the indicator electrode (a bright platinum wire or piece of platinum foil) to the positive post; this is exactly the reverse of the way the connections were made with the hydrogen electrode. During the titration, at about $p\mathrm{H} = 7$, the solution begins to turn brown and the electrode becomes unsteady. At this point reverse the electrodes and continue the titration. During the first part of the titration the hydroquinone (quinol) is being formed by reduction, but when the electrodes are connected in the opposite way the quinol is being oxidized to quinone.

With the quinhydrone electrode, the pH values cannot be read directly with the instrument which has been described but must be computed at 25° by the formula

$$p\mathrm{H} = \frac{0.367 - \text{observed potential difference}}{0.059}$$

The value 0.367 is the difference in potential between the hydroquinone electrode in a molal solution of H^+ (+0.705 volt) and that of the 0.1 N calomel solution (+0.338 volt). Care must be taken to remember that when the indicator electrode is positive to the calomel, the observed voltages are to be given the positive sign in this formula, but when the connections are reversed they should be used with the negative sign; that is, the observed reading is to be added to 0.367.[1]

With the quinhydrone electrode the solution can be stirred vigorously while the readings are being made, and the state of equilibrium is reached with astonishing rapidity. Usually 5 seconds is long enough to wait before taking a reading after the addition of reagent. If in an acid-base titration the end point alone is desired, a complete titration can often be made in 5 minutes. For these reasons, the quinhydrone electrode has become very popular in industrial work. The outfit shown in Fig. 48 is suitable for these titrations and is less expensive than the hydrogen-ion potentiometer that has been described.

To prepare quinhydrone, dissolve 25 g of quinol in 100 ml of water, heat to 65°, and mix with a solution of 100 g of ferric-ammonium-alum dissolved in 300 ml of water at 65°. Heat the two solutions separately and mix at 65°. Then cool the mixture in ice. A large mass of violet needle-shaped crystals will separate from the solution. Filter off the crystals, drain with suction, and wash with small portions of ice-water. Transfer the crystals, as soon as possible, to a glass-stoppered bottle of dark glass. For the titrations use a freshly prepared, saturated solution of quinhydrone in water, preparing only 10 ml of the solution at a time. Use about 4 drops of the saturated alcoholic solution in the solution to be titrated.

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[1] Using a *saturated* calomel electrode at 25°, the formula becomes $p\mathrm{H} = \frac{0.453 - V}{0.059}$. The potential of the quinhydrone electrode is equal to the saturated calomel electrode at $p\mathrm{H} = 7.67$.

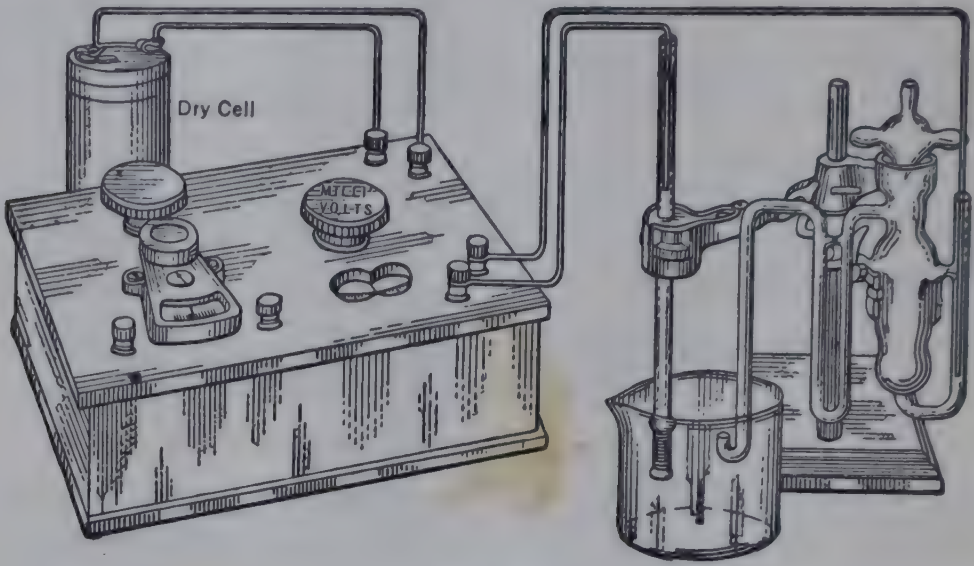


Fig. 48.

The quinhydrone electrode is not suitable for the accurate determination of pH values in alkaline solutions; the solubility of the quinhydrone is greater than in acid solutions, the equality in the concentrations of quinone and hydroquinone is no longer maintained, and the measured voltage is no longer a linear function of the pH value of the solution.

The Glass Electrode. Today many pH determinations are made with the so-called *glass electrode.* The idea can be traced back to Walther Nernst, who, in 1892, thought that a difference in potential should exist between a solid solution and a saturated solution. Since glass is a solid solution, Haber reasoned that a difference in potential should exist when a thin wall of glass is interposed between two aqueous solutions, and he was able to carry out acid-base titrations by measuring the potential between a solution of known pH and that of the solution being titrated. Since then much work has been done along these lines. The potential difference at the very thin wall of glass varies with different kinds of glass and many kinds of glass have proved unsuitable. Special glass can now be purchased for making glass electrodes and also the complete assembly can be purchased.

The resistance of the glass membrane is high so that the usual galvanometer should be replaced with a vacuum-tube amplifier circuit and potentiometer. The glass electrode is sometimes a little erratic through sluggishness in the attainment of equilibrium with the solution under test, and the actual potential differences are not always exactly the values expected; but excellent work can be done with it and its popularity seems to be increasing.

If we have a saturated calomel cell in contact with an acid solution of known pH separated by glass from another solution of unknown pH which is also in contact with another saturated calomel cell, the potential difference between the two calomel cells will change in accordance with the Nernst rule as the concentration of hydrogen ions is changed in the unknown cell. We can assume that the potential differences remain constant except in the solution being measured.

For the solution inside the glass electrode various recommendations have been made. Thus 0.1 *N* HCl, quinhydrone in *N* HCl, 0.05 *M* potassium acid phthallate solution, and potassium tetroxalate solution have been used. It has also been recommended that the solution of known pH be replaced with silver/silver chloride in a chloride buffer. With a film made of Corning No. 015 glass and with quinhydrone in 0.1 *N* HCl we have

$$p\text{H} = K + \frac{E}{0.060} \quad \text{at } 30°$$

in which K is a constant. With the glass electrode containing a *normal* calomel cell on one side and a Ag|AgCl|*N* HCl cell on the other we have at 30°

$$p\text{H} = \frac{E + 0.0724}{0.06}$$

and when a saturated calomel cell is used,

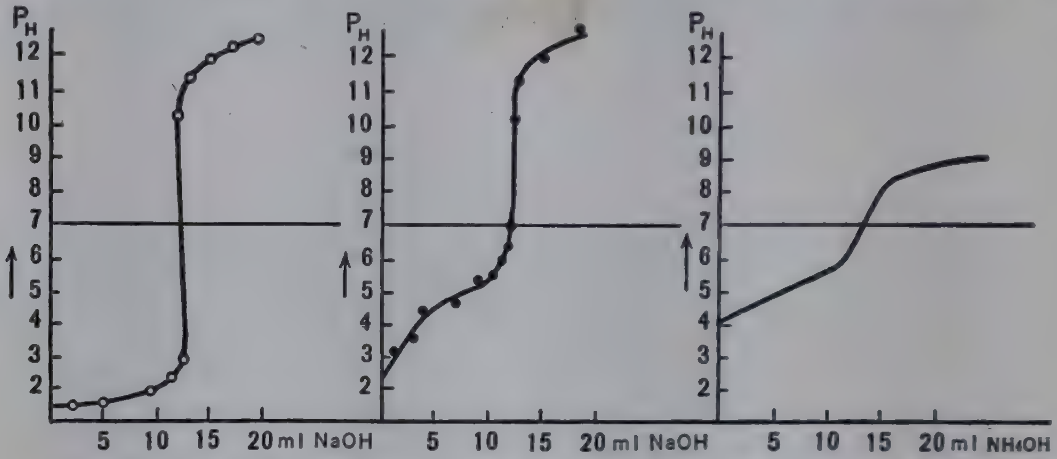
$$p\text{H} = \frac{E + 0.1066}{0.060}$$

The advantages of the glass electrode are: (1) independence of the presence of oxidizing or reducing agents; (2) use of very small volumes of solutions; (3) no substance need be added to the solution tested. Disadvantages are its fragility, its high electrical resistance, and the fact that it will not give accurate pH values in solutions more basic than about pH 9.5.

The hydrogen electrode, the quinhydrone electrode, and the glass electrode are much used for determining the pH of solutions. They can also be used to determine the pH at which the end point of a neutralization reaction takes place, whereby the most suitable indicator can be chosen. Finally, they can be used for titration of an acid against a base, and *vice versa.*

Potential during a Titration. When an acid is titrated with a standard solution of a base, the potential of the hydrogen electrode does not usually change very fast until the vicinity of the end point is reached. When the end point is near, it is best to take readings regularly after additions of small portions of the reagent. Each time a reading is made, record the buret reading and the observed voltage. When the voltages are plotted as ordinates against the buret readings as abscissas, curves like those shown in Fig. 49 will be obtained. The end point is at the place where there is a sudden change in direction of the curve, and the corresponding *p*H is halfway up the vertical lines shown in the titration curves.

It is clear that the method is more tedious than that of a titration with indicators but the end point is obtained irrespective of the color of the solution. Two and sometimes three acids can be titrated in the presence of one another provided that their ionization constants are far enough apart. For phosphoric acid the ionization constants are far enough apart ($K_1 = 1.1 \times 10^{-2}$; $K_2 = 2.0 \times 10^{-7}$; $K_3 = 3.6 \times 10^{-13}$) so that three end points can be obtained with sodium hydroxide, the first corresponding to the formation of NaH_2PO_4 at about $p\text{H} = 3$, the second corresponding to the formation of Na_2HPO_4 at about $p\text{H} = 9$, and the third corresponding to the formation of Na_3PO_4 at about $p\text{H} = 13$.



Titration of 0.1 *N* HCl with 0.1 *N* NaOH

Titration of 0.1 *N* $HC_2H_3O_2$ with 0.1 *N* NaOH

Titration of 0.1 *N* $HC_2H_3O_2$ with 0.1 *N* NH_4OH

FIG. 49.

While titrating with a saturated calomel electrode and fairly wide opening, it is well to flush out the tip of the capillary by adding fresh saturated potassium chloride to the electrode vessel every other time that a reading is made. When the titration is finished, plot the potentials, after deducting the value of the calomel electrode, as ordinates, with the buret readings as abscissas.

Sources of Error. One of the difficulties likely to be encountered is the *polarizing* of the platinized electrode. When making a reading, if the key is held closed with the potentiometer not yet balanced, an appreciable current will flow and the electrode becomes polarized. This can be detected by taking two readings at the same point. By waiting a few minutes, a correct reading can be obtained, whereas the reading will be low if there is polarization.

The electrode is also likely to become *poisoned*, particularly when the solution contains ammonia or hydrogen sulfide. This can be detected by a peculiar drift in the galvanometer, a tendency for the needle to move to one side after a balance has apparently been reached. A poisoned electrode must be cleaned and replatinized.

The tip of the calomel electrode should be flushed frequently to remove solution that has diffused up into the tubing. This can be avoided and an error due to liquid potentials overcome by means of a " salt bridge." Have the tip of the calomel electrode dip into a beaker containing a saturated solution of potassium chloride and have the beaker connected with the titration beaker by means of glass tubing, containing the saturated potassium chloride solution.

Care should be taken to exclude all carbon dioxide and oxygen from the Kipp generator every time the outlet tube has been left exposed.

Oxidation-Reduction Reactions. Not only the metals can be arranged in a potential series but every oxidation reaction finds a place in the table. Numerous oxidation reactions have been studied electrometrically with a set-up like that described for use when quinhydrone was employed as indicator of acidity or alkalinity. The indicator electrode is a bright piece of platinum wire or foil and never one that is coated with platinum black. Usually the calomel electrode is connected to the negative binding post just as at the start of the titration with quinhydrone. Just as a mixture of two acids can be titrated potentiometrically and two, or even more, end points determined, so two or more end points can often be obtained in titrating, say, with potassium dichromate or with potassium permanganate.

In the determination of iron in limonite, for example, the sample can be dissolved in hydrochloric acid and the resulting ferric chloride reduced by adding stannous chloride. It is then quite unnecessary to remove the excess of stannous chloride; the solution can be diluted and titrated immediately with, say, potassium dichromate solution. The first sudden change in the titration curve will correspond to the oxidation of the excess stannous chloride, and the second to the complete oxidation of the ferrous chloride; and the volume of dichromate solution used between these two end points corresponds to the quantity of iron salt present in the solution. The titration of ferrous salts with permanganate in hydrochloric acid solutions can also be accomplished potentiometrically.

Figures 50 and 51 are some curves obtained by a sophomore student while this book was being written.

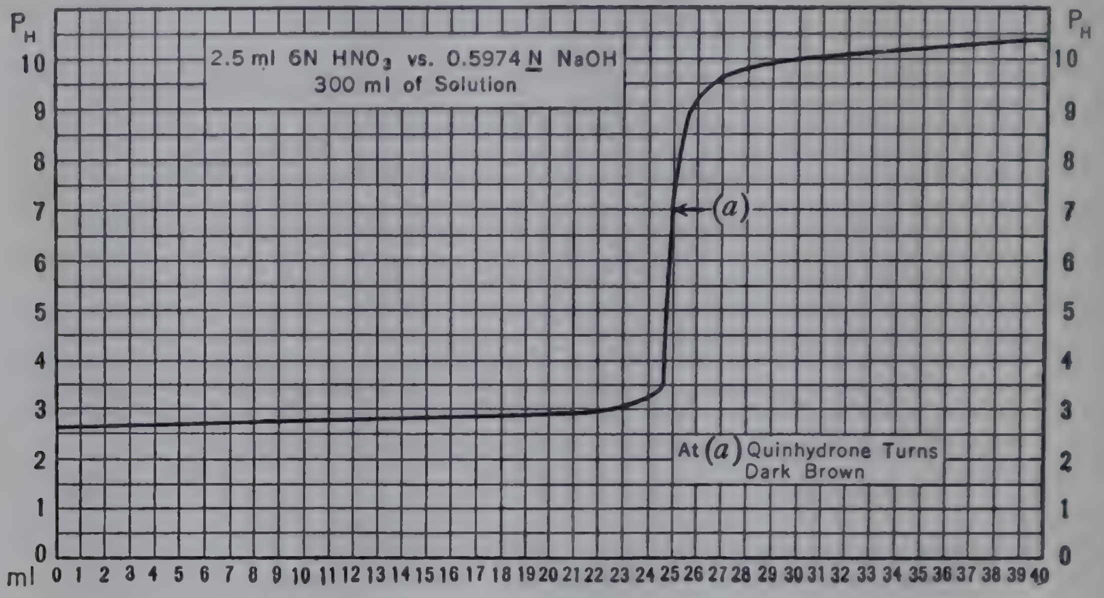


FIG. 50.

Buffered Solutions of Definite *p*H Values[1]

Prepare 0.2 molal solutions of:

A. $Na_2HPO_4 \cdot 2H_2O$. Formed by exposing powdered $Na_2HPO_4 \cdot 12H_2O$ to the air in an open dish for several weeks. Dissolve 35.6 g in water and dilute to 1 l.

B. $H_3C_6H_5O_7 \cdot H_2O$. Dissolve 42.0 g of citric acid in water and dilute to 1 l.

C. NaOH. Standardize against the citric acid solution using phenolphthalein as indicator. Ten milliliters of the citric acid should neutralize 30 ml of the sodium hydroxide.

To obtain solutions of definite *p*H values mix as follows:

*p*H = 4. Mix 77.1 ml of A with 122.9 ml of B.
*p*H = 5. Mix 103.0 ml of A with 97.0 ml of B.
*p*H = 6. Mix 126.3 ml of A with 73.7 ml of B.
*p*H = 7. Mix 164.7 ml of A with 35.3 ml of B.
*p*H = 8. Mix 194.5 ml of A with 5.5 ml of B.
*p*H = 9. Mix 50 ml of C with 21.3 ml of D. Dilute to 200 ml.
*p*H = 10. Mix 50 ml of C with 43.9 ml of D. Dilute to 200 ml.

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[1] Clark, *Determination of Hydrogen-Ion Concentration.*

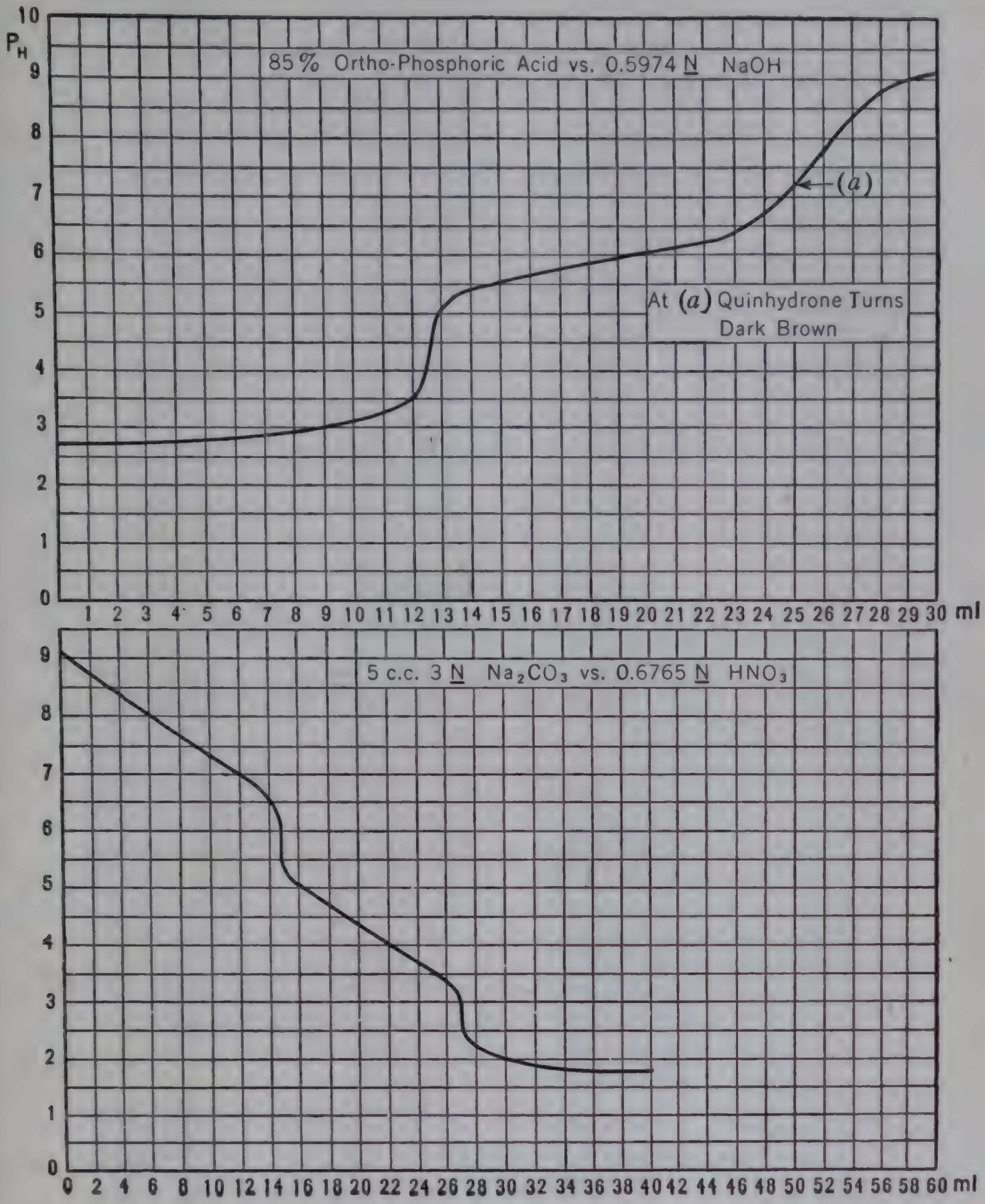

FIG. 51.

Suggested Laboratory Work

1. Connect the apparatus as shown in Fig. 47. Instead of the expensive potentiometer, a slide-wire bridge 1 meter long and with a resistance of 100 ohms can be used with fairly good results. Calibrate the bridge against a standard cell and with connections as shown in Fig. 46. If a sensitive galvanometer is used, fairly good results can be obtained.

2. Prepare the calomel electrode, a supply of tenth-normal potassium chloride and a buffer solution (see p. 325).

3. Test the buffer solution and estimate the *p*H value.

4. Titrate a solution of hydrochloric acid with tenth-normal sodium hydroxide using first the hydrogen electrode and then the quinhydrone electrode.

5. Determine the iron content of an ore by a procedure similar to that given on p. 325 but without removing the excess stannous chloride with mercuric chloride solution.

6. Analyze a solution of sodium hydroxide and sodium carbonate, or a solution of sodium carbonate and sodium bicarbonate, or a solution of phosphoric acid and sodium dihydrogen phosphate, or a solution of monosodium phosphate and disodium phosphate, or a solution of disodium phosphate and trisodium phosphate.

HOME PROBLEMS

77. Plot, with millivolts of electrode potential as ordinates against milliliters of NaOH as abscissas, a curve for the titration of 20.0 ml of 0.1 *N* HCl with 0.1 *N* NaOH, showing when the solution is exactly neutral and when the desired end point occurs, using the following data:

ml	0.0	4.0	8.0	12.0	16.0	18.0	19.0	19.5	19.8	20.0
mv	350	355	370	390	427	450	480	515	550	690
ml	20.2	20.5	21.0	22.0	24.0	28.0	32.0			
mv	840	875	900	930	948	970	985			

78. Plot in the same way (on the same sheet) the titration of 20.0 ml of 0.1 *N* acetic acid with 0.1 *N* NaOH using the following data:

ml	0.0	4.0	8.0	12.0	16.0	18.0	19.0	19.5	19.8	20.0
mv	420	475	540	588	620	638	650	670	790	830
ml	20.2	20.5	21.0	22.0	24.0	28.0	32.0			
mv	856	875	900	930	948	970	985			

Explain the differences between this graph and that of the previous problem.

79. Plot in the same way the titration of 0.6000 g of Na_2CO_3 in 200 ml of boiled water using 0.4 *N* HCl at 25° from the following data:

ml	0.0	5.0	10.0	15.0	18.0	19.0	20.0	21.0	22.0	25.0	30.0
mv	916	855	838	794	777	765	740	704	680	661	630
ml	35.0	40.0	40.5	41.0	41.5	42.0	43.0	45.0	50.0		
mv	602	565	550	455	416	400	390	370	360		

80. Similarly make a plot for the titration of 40 ml of 0.2133 *N* H_3PO_4 diluted with water to 200 ml and titrated with 0.2 *N* NaOH at 25°. Show the *p*H at which the saturation of the first and second H ions of H_3PO_4 occur.

ml	0	5	10	13.01	13.5	13.8	14.0	14.2	14.4	14.8	15.5
mv	300	315	350	385	398	405	415	450	525	555	565
ml	17.0	20.0	25.0	27.5	28.5	28.8	29.0	29.2	29.5	30.0	31.0
mv	580	603	640	658	675	685	740	760	795	815	835
ml	35.0	40.0									
mv	870	890									

In solving the following problems bear in mind that phenolphthalein changes color at $p\text{H} = 9$ and methyl orange at $p\text{H} = 4$.

81. How many milliliters of 0.1 N NaOH must be added to 1 l of water to cause it to turn 0.03 ml of 1 per cent phenolphthalein in the solution pink?

82. If a solution contains NH_4OH to make it 0.001 N as a base and is 0.1 N in NH_4Cl, what color would you expect on adding a drop of phenolphthalein to one portion and a drop of methyl orange to another? The ionization constant of NH_4OH can be taken as 1.8×10^{-5}, and the NH_4Cl can be regarded as all ionized.

83. In titrating 50 ml of 0.5016 N NaOH (diluted to 200 ml) with 0.5 N HCl and using phenolphthalein as indicator, find the percentage error caused by the fact that the indicator change does not occur at exactly $p\text{H} = 7$.

Assuming that the buret readings are good to ±0.02 ml and that the normal concentration of the NaOH is accurate to 1 part in 1000, what would be the precision of this titration for establishing the N concentration of the HCl if the color changes can be reproduced with volumes agreeing within ±0.04 ml and no other errors are to be considered?

84. A 0.1 N solution of Na salt of a weak monobasic acid gives a rose transition tint when a few drops of phenolphthalein are added but remains colorless with a few drops of thymolphthalein (this indicator starts to turn from colorless to blue at $p\text{H}$ 10). Calculate approximate degree of hydrolysis of the salt.

85. Two hundred fifty milliliters of $KMnO_4$ titrated with 0.1076 N Mohr's salt solution gave the following data:

ml	0.0	5.0	10.0	15.0	20.0	21.0	21.5	22.0	22.2	22.4	23.0	25.0
mv	720	745	756	762	770	771	770	768	450	390	350	off scale

Plot the titration curve and determine N of $KMnO_4$.

86. The Cr in 5 g of steel was oxidized to chromate and then titrated electrometrically with 0.1039 N copperas solution. Compute the percentage of chromium from the following data:

ml	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	36.0	37.0	37.5	38.0	38.3
mv	650	790	800	810	820	840	860	878	885	887	887	885	884
ml	38.4	39.0	40.0	45.0									
mv	503	445	415	390									

COMPARISON OF METRIC AND CUSTOMARY UNITS (U.S.)

LENGTH

1 millimeter, mm = 0.03937 inch.	1 inch = 25.4 millimeters.
1 centimeter, cm = 0.39371 inch.	1 inch = 2.5400 centimeters.
1 meter, m = 3.2808 feet.	1 foot = 0.30480 meter.
1 meter = 1.0936 yards.	1 yard = 0.91440 meter.
1 kilometer = 0.62137 (U.S.) mile.	1 mile = 1.6094 kilometers.

AREAS

1 square millimeter, sq mm = 0.00155 sq in.	1 sq in = 645.16 sq mm.
1 square centimeter, sq cm = 0.1550 sq in.	1 sq in = 6.452 sq cm.
1 square meter, sq m = 10.764 sq ft.	1 sq ft = 0.0929 sq m.
1 square meter = 1.196 sq yd.	1 sq yd = 0.8361 sq m.
1 square kilometer = 0.3861 sq mi.	1 sq mi = 2.5900 sq km.
1 hectare = 2.471 acres.	1 acre = 0.4047 hectare.

VOLUMES

1 cubic millimeter, cu mm = 0.000061 cu in.	1 cu in = 16,387 cu mm.
1 cubic centimeter, ml = 0.06103 cu in.	1 cu in = 16.387 ml.
1 cubic meter = 35.314 cu ft.	1 cu ft = 0.02832 cu m.
= 61,028 cu in.	= 28.32 liters.
1 cubic meter = 1.3079 cu yd.	1 cu yd = 0.7645 cu m.

CAPACITIES

1 cubic centimeter, ml = 0.03381 (U.S.) liquid oz.	1 ounce = 29.574 ml.
1 cubic centimeter = 0.2705 (U.S.) apothecaries' dram.	1 dram = 3.6967 ml.
1 cubic centimeter = 0.8115 (U.S.) apothecaries' scruple.	1 scruple = 1.2322 ml.
1 liter = 1.05668 (U.S.) liquid qt.	1 quart = 0.94636 liter.
1 liter = 0.26417 (U.S.) gallon.	1 gallon = 3.78543 liters.
1 liter = 0.11351 (U.S.) peck.	1 peck = 8.80982 liters.
1 hectoliter = 2.83774 (U.S.) bushels.	1 bushel = 0.35239 hectoliter.

MASSES

1 gram = 15.432 grains.	1 grain = 0.06480 gram.
1 gram = 0.03527 avoirdupois ounce.	1 ounce (av.) = 28.350 grams = 437.5 grains.
1 gram = 0.03215 troy ounce.	1 ounce (troy) = 31.103 grams = 480 grains.
1 kilogram = 2.2046 pounds (av.).	1 pound (av.) = 0.4536 kilogram.
1 kilogram = 2.6792 pounds (troy).	1 pound (troy) = 0.37324 kilogram.

AVOIRDUPOIS WEIGHT

The system of weights in ordinary use by which common or heavy articles are weighed.

16 drams = 1 ounce = 28.35 grams.
16 ounces = 1 pound = 453.59 grams.
25 pounds = 1 quarter = 11.34 kilograms.
4 quarters = 1 hundred weight = 45.359 kilograms.

APOTHECARIES' WEIGHT

The system of weights sometimes employed in weighing medicines.

1 grain = 0.0648 gram.
20 grains = 1 scruple = 1.296 grams.
3 scruples = 1 drachm = 3.888 grams.
8 drachms = 1 ounce = 31.10 grams.
12 ounces = 1 pound = 373.23 grams.
1 apothecaries' (or troy) pound contains 5760 grains.
1 apothecaries' (or troy) ounce contains 480 grains.

FLUID MEASURE

1 minim = 0.06161 cubic centimeter.
60 minims = 1 fluid drachm = 3.696 cubic centimeters.
8 fluid drachms = 1 fluid ounce = 29.573 cubic centimeters.
16 fluid ounces = 1 U.S. pint = 473.18 cubic centimeters.
8 pints = 1 U.S. gallon = 3.785 liters.
1 U.S. gallon contains 231 cubic inches.

The minim, fluid drachm, fluid ounce and pint are the fluid measures sometimes employed by apothecaries.

1 U.S. gallon of water = 8.64 lbs.

Useful Approximations

1 molecular weight in grams of a gas = 22.4 liters.
1 molecular weight in pounds of a gas = 359 cubic feet.

To find temperatures on the absolute scales, which starts at the "absolute" zero, add 273° to the reading of the Centigrade thermometer or 459.4° to the reading of the Fahrenheit thermometer. The so-called "standard conditions" for measuring gases (0° and 760 mm of Hg pressure) are 273° (absolute) and 760 mm or 491.4° F. (absolute) and 29.92 inches of mercury pressure or 14.7 pounds per square inch.

SPECIFIC GRAVITIES OF COMMON SUBSTANCES

Aluminum	2.7	Lead	11.3	Quartz	2.66
Brass	8.4	Marble	2.7	Rock Salt	2.15
Cast iron	7.3	Mercury	13.6	Silver	10.5
Glass	2.6	Nickel	8.7	Steel	7.8
Gold	19.3	Platinum	21.4	Sulfur	2.05
Ivory	1.9	Porcelain	2.4	Zinc	7.10

Common Laboratory Reagents

In analytical directions, the concentration of a solution is sometimes designated by the density, sometimes by the normality, and sometimes by the percentage of active reagent present. In the case of acids and bases the percentage of active reagent is always based on the weight of the solution. In the case of salt solutions, the chemist is usually careless and calls, for example, a 10 per cent solution one that contains 10 g of solid per 100 ml.

Reagent	Normal Concn.	Density	1 ml Contains	Preparation
Acetic acid (glacial)	17.5 *N*	1.06	1.06 g $HC_2H_3O_2$	Purchased
Acetic acid (diluted)	6 *N*	1.05	0.36 g $HC_2H_3O_2$	Mix 350 ml of glacial acetic acid with 650 ml of water
Ammonium hydroxide (concentrated)	15 *N*	0.90	0.26 g NH_3	Purchased
Ammonium hydroxide (diluted)	6 *N*	0.96	0.10 g NH_3	Mix 400 ml of strong NH_4OH with 600 ml of water
Hydrochloric acid (concentrated)	12 *N*	1.19	0.43 g HCl	Purchased
Hydrochloric acid (diluted)	6 *N*	1.1	0.22 g HCl	Mix the concentrated acid with an equal volume of water
Hydrofluoric acid	27 *N*	1.15	0.55 g HF and H_2F_2	Purchased in ceresin bottles
Nitric acid (concentrated)	15.7 *N*	1.42	0.99 g HNO_3	Purchased
Nitric acid (diluted)	6 *N*	1.20	0.38 g HNO_3	Mix 380 ml of concentrated acid with 620 ml of water
Phosphoric acid	15 *M*	1.71	1.45 g H_3PO_4	Purchased
Sulfuric acid (concentrated)	36 *N*	1.84	1.76 g H_2SO_4	Purchased
Sulfuric acid (diluted)	18 *N*	1.49	0.88 g H_2SO_4	Pour 465 ml of concentrated acid into 535 ml of water
Sulfuric acid (diluted)	6 *N*	1.18	0.29 g H_2SO_4	Pour 200 ml of concentrated acid into 1 l of water

TENSION OF WATER VAPOR ACCORDING TO REGNAULT

Degrees, C	Tension in Millimeters	Degrees, C	Tension in Millimeters	Degrees, C	Tension in Millimeters
−2.0	3.955	+2.0	5.302	+6.0	6.998
1.9	3.985	2.1	5.340	6.1	7.047
1.8	4.016	2.2	5.378	6.2	7.095
1.7	4.047	2.3	5.416	6.3	7.144
1.6	4.078	2.4	5.454	6.4	7.193
1.5	4.109	2.5	5.491	6.5	7.242
1.4	4.140	2.6	5.530	6.6	7.292
1.3	4.171	2.7	5.569	6.7	7.342
1.2	4.203	2.8	5.608	6.8	7.392
1.1	4.235	2.9	5.647	6.9	7.442
1.0	4.267	3.0	5.687	7.0	7.492
0.9	4.299	3.1	5.727	7.1	7.544
0.8	4.331	3.2	5.767	7.2	7.595
0.7	4.364	3.3	5.807	7.3	7.647
0.6	4.397	3.4	5.848	7.4	7.699
0.5	4.430	3.5	5.889	7.5	7.751
0.4	4.463	3.6	5.930	7.6	7.804
0.3	4.497	3.7	5.972	7.7	7.857
0.2	4.531	3.8	6.014	7.8	7.910
0.1	4.565	3.9	6.055	7.9	7.964
0.0	4.600	4.0	6.097	8.0	8.017
+0.1	4.633	4.1	6.140	8.1	8.072
0.2	4.667	4.2	6.183	8.2	8.126
0.3	4.700	4.3	6.226	8.3	8.181
0.4	4.733	4.4	6.270	8.4	8.236
0.5	4.767	4.5	6.313	8.5	8.291
0.6	4.801	4.6	6.357	8.6	8.347
0.7	4.836	4.7	6.401	8.7	8.404
0.8	4.871	4.8	6.445	8.8	8.461
0.9	4.905	4.9	6.490	8.9	8.517
1.0	4.940	5.0	6.534	9.0	8.574
1.1	4.975	5.1	6.580	9.1	8.632
1.2	5.011	5.2	6.625	9.2	8.690
1.3	5.047	5.3	6.671	9.3	8.748
1.4	5.082	5.4	6.717	9.4	8.807
1.5	5.118	5.5	6.763	9.5	8.865
1.6	5.155	5.6	6.810	9.6	8.925
1.7	5.191	5.7	6.857	9.7	8.985
1.8	5.228	5.8	6.904	9.8	9.045
1.9	5.265	5.9	6.951	9.9	9.105

TENSION OF WATER VAPOR ACCORDING TO REGNAULT — *Continued*

Degrees, C	Tension in Millimeters	Degrees, C	Tension in Millimeters	Degrees, C	Tension in Millimeters
+10.0	9.165	+14.0	11.908	+18.0	15.357
10.1	9.227	14.1	11.986	18.1	15.454
10.2	9.288	14.2	12.064	18.2	15.552
10.3	9.350	14.3	12.142	18.3	15.650
10.4	9.412	14.4	12.220	18.4	15.747
10.5	9.474	14.5	12.298	18.5	15.845
10.6	9.537	14.6	12.378	18.6	15.945
10.7	9.601	14.7	12.458	18.7	16.045
10.8	9.665	14.8	12.538	18.8	16.145
10.9	9.728	14.9	12.619	18.9	16.246
11.0	9.792	15.0	12.699	19.0	16.346
11.1	9.857	15.1	12.781	19.1	16.449
11.2	9.923	15.2	12.864	19.2	16.552
11.3	9.989	15.3	12.947	19.3	16.655
11.4	10.054	15.4	13.029	19.4	16.758
11.5	10.120	15.5	13.112	19.5	16.861
11.6	10.187	15.6	13.197	19.6	16.967
11.7	10.255	15.7	13.281	19.7	17.073
11.8	10.322	15.8	13.366	19.8	17.179
11.9	10.389	15.9	13.451	19.9	17.285
12.0	10.457	16.0	13.536	20.0	17.391
12.1	10.526	16.1	13.623	20.1	17.500
12.2	10.596	16.2	13.710	20.2	17.608
12.3	10.665	16.3	13.797	20.3	17.717
12.4	10.734	16.4	13.885	20.4	17.826
12.5	10.804	16.5	13.972	20.5	17.935
12.6	10.875	16.6	14.062	20.6	18.047
12.7	10.947	16.7	14.151	20.7	18.159
12.8	11.019	16.8	14.241	20.8	18.271
12.9	11.090	16.9	14.331	20.9	18.383
13.0	11.162	17.0	14.421	21.0	18.495
13.1	11.235	17.1	14.513	21.1	18.610
13.2	11.309	17.2	14.605	21.2	18.724
13.3	11.383	17.3	14.697	21.3	18.839
13.4	11.456	17.4	14.790	21.4	18.954
13.5	11.530	17.5	14.882	21.5	19.069
13.6	11.605	17.6	14.977	21.6	19.187
13.7	11.681	17.7	15.072	21.7	19.305
13.8	11.757	17.8	15.167	21.8	19.423
13.9	11.832	17.9	15.262	21.9	19.541

TENSION OF WATER VAPOR ACCORDING TO REGNAULT—*Concluded*

Degrees, C	Tension in Millimeters	Degrees, C	Tension in Millimeters	Degrees, C	Tension in Millimeters
+22.0	19.659	+26.5	25.738	+31.0	33.405
22.1	19.780	26.6	25.891	31.1	33.596
22.2	19.901	26.7	26.045	31.2	33.787
22.3	20.022	26.8	26.198	31.3	33.980
22.4	20.143	26.9	26.351	31.4	34.174
22.5	20.265	27.0	26.505	31.5	34.368
22.6	20.389	27.1	26.663	31.6	34.564
22.7	20.514	27.2	26.820	31.7	34.761
22.8	20.639	27.3	26.978	31.8	34.959
22.9	20.763	27.4	27.136	31.9	35.159
23.0	20.888	27.5	27.294	32.0	35.359
23.1	21.016	27.6	27.455	32.1	35.559
23.2	21.144	27.7	27.617	32.2	35.760
23.3	21.272	27.8	27.778	32.3	35.962
23.4	21.400	27.9	27.939	32.4	36.165
23.5	21.528	28.0	28.101	32.5	36.370
23.6	21.659	28.1	28.267	32.6	36.576
23.7	21.790	28.2	28.433	32.7	36.783
23.8	21.921	28.3	28.599	32.8	36.991
23.9	22.053	28.4	28.765	32.9	37.200
24.0	22.184	28.5	28.931	33.0	37.410
24.1	22.319	28.6	29.101	33.1	37.621
24.2	22.453	28.7	29.271	33.2	37.832
24.3	22.588	28.8	29.441	33.3	38.045
24.4	22.723	28.9	29.612	33.4	38.258
24.5	22.858	29.0	29.782	33.5	38.473
24.6	22.996	29.1	29.956	33.6	38.689
24.7	23.135	29.2	30.131	33.7	38.906
24.8	23.273	29.3	30.305	33.8	39.124
24.9	23.411	29.4	30.479	33.9	39.344
25.0	23.550	29.5	30.654	34.0	39.565
25.1	23.692	29.6	30.833	34.1	39.786
25.2	23.834	29.7	31.011	34.2	40.007
25.3	23.976	29.8	31.190	34.3	40.230
25.4	24.119	29.9	31.369	34.4	40.455
25.5	24.261	30.0	31.548	34.5	40.680
25.6	24.406	30.1	31.729	34.6	40.907
25.7	24.552	30.2	31.911	34.7	41.135
25.8	24.697	30.3	32.094	34.8	41.364
25.9	24.842	30.4	32.278	34.9	41.595
26.0	24.988	30.5	32.463	35.0	41.827
26.1	25.138	30.6	32.650		
26.2	25.288	30.7	32.837		
26.3	25.438	30.8	33.026		
26.4	25.588	30.9	33.215		

DENSITY OF ACETIC ACID AT 15°

Specific Gravity	Per Cent $H.C_2H_3O_2$	Specific Gravity	Per Cent $H.C_2H_3O_4$	Specic Gravity	Per Cent $H.C_3H_2O_2$	Specific Gravity	Per Cent $H.C_2H_3O$
0.9992	0	1.0363	26	1.0623	51	1.0747	76
1.0007	1	1.0375	27	1.0631	52	1.0748	77
1.0022	2	1.0388	28	1.0638	53	1.0748	78
1.0037	3	1.0400	29	1.0646	54	1.0748	79
1.0052	4	1.0412	30	1.0653	55	1.0748	80
1.0067	5	1.0424	31	1.0660	56	1.0747	81
1.0083	6	1.0436	32	1.0666	57	1.0746	82
1.0098	7	1.0447	33	1.0673	58	1.0744	83
1.0113	8	1.0459	34	1.0679	59	1.0742	84
1.0127	9	1.0470	35	1.0685	60	1.0739	85
1.0142	10	1.0481	36	1.0691	61	1.0736	86
1.0157	11	1.0492	37	1.0697	62	1.0731	87
1.0171	12	1.0502	38	1.0702	63	1.0726	88
1.0185	13	1.0513	39	1.0707	64	1.0720	89
1.0200	14	1.0523	40	1.0712	65	1.0713	90
1.0214	15	1.0533	41	1.0717	66	1.0705	91
1.0228	16	1.0543	42	1.0721	67	1.0696	92
1.0242	17	1.0552	43	1.0725	68	1.0686	93
1.0256	18	1.0562	44	1.0729	69	1.0674	94
1.0270	19	1.0571	45	1.0733	70	1.0660	95
1.0284	20	1.0580	46	1.0737	71	1.0644	96
1.0298	21	1.0589	47	1.0740	72	1.0625	97
1.0311	22	1.0598	48	1.0742	73	1.0604	98
1.0324	23	1.0607	49	1.0744	74	1.0580	99
1.0337	24	1.0615	50	1.0746	75	1.0553	100
1.0350	25						

DENSITY OF PHOSPHORIC ACID AT 17.5°

Specific Gravity	Per Cent P_2O_5	Per Cent H_3PO_4	Specific Gravity	Per Cent P_2O_5	Per Cent H_3PO_4	Specific Gravity	Per Cent P_2O_5	Per Cent H_3PO_4
1.809	68.0	93.67	1.462	46.0	63.37	1.208	24.0	33.06
1.800	67.5	92.99	1.455	45.5	62.68	1.203	23.5	32.37
1.792	67.0	92.30	1.448	45.0	61.99	1.198	23.0	31.68
1.783	66.5	91.61	1.441	44.5	61.30	1.193	22.5	30.99
1.775	66.0	90.92	1.435	44.0	60.61	1.188	22.0	30.31
1.766	65.5	90.23	1.428	43.5	59.92	1.183	21.5	29.62
1.758	65.0	89.54	1.422	43.0	59.23	1.178	21.0	28.93
1.750	64.5	88.85	1.415	42.5	58.55	1.174	20.5	28.24
1.741	64.0	88.16	1.409	42.0	57.86	1.169	20.0	27.55
1.733	63.5	87.48	1.402	41.5	57.17	1.164	19.5	26 86
1.725	63.0	86.79	1.396	41.0	56.48	1.159	19.0	26.17
1.717	62.5	86.10	1.389	40.5	55.79	1.155	18.5	25.48
1.709	62.0	85.41	1.383	40.0	55.10	1.150	18.0	24.80
1.701	61.5	84.72	1.377	39.5	54.41	1.145	17.5	24.11
1.693	61.0	84.03	1.371	39.0	53.72	1.140	17.0	23.42
1.685	60.5	83.34	1.365	38.5	53.04	1.135	16.5	22.73
1.677	60.0	82.65	1.359	38.0	52.35	1.130	16.0	22.04
1.669	59.5	81.97	1.354	37.5	51.66	1.126	15.5	21.35
1.661	59.0	81.28	1.348	37.0	50.97	1.122	15.0	20.66
1.653	58.5	80.59	1.342	36.5	50.28	1.118	14.5	19.97
1.645	58.0	79.90	1.336	36.0	49.59	1.113	14.0	19.28
1.637	57.5	79.21	1.330	35.5	48.90	1.109	13.5	18.60
1.629	57.0	78.52	1.325	35.0	48.21	1.104	13.0	17.91
1.621	56.5	77.83	1.319	34.5	47.52	1.100	12.5	17.22
1.613	56.0	77.14	1.314	34.0	46.84	1.096	12.0	16.53
1.605	55.5	76.45	1.308	33.5	46.15	1.091	11.5	15 84
1.597	55.0	75.77	1.303	33.0	45.46	1.087	11.0	15.15
1.589	54.5	75.08	1.298	32.5	44.77	1.083	10.5	14.46
1.581	54.0	74.39	1.292	32.0	44.08	1.079	10.0	13.77
1.574	53.5	73.70	1.287	31.5	43.39	1.074	9.5	13.09
1.566	53.0	73.01	1.281	31.0	42.70	1.070	9.0	12.40
1.559	52.5	72.32	1.276	30.5	42.01	1.066	8.5	11.71
1.551	52.0	71.63	1.271	30.0	41.33	1.062	8.0	11.02
1.543	51.5	70.94	1.265	29.5	40.64	1.058	7.5	10.33
1.536	51.0	70.26	1.260	29.0	39.95	1.053	7.0	9.64
1.528	50.5	69.57	1.255	28.5	39.26	1.049	6.5	8.95
1.521	50.0	68.88	1.249	28.0	38.57	1.045	6.0	8.26
1.513	49.5	68.19	1.244	27.5	37.88	1.041	5.5	7.57
1.505	49.0	67.50	1.239	27.0	37.19	1.037	5.0	6.89
1.498	48.5	66.81	1.233	26.5	36.50	1.033	4.5	6.20
1.491	48.0	66.12	1.228	26.0	35.82	1.029	4.0	5.51
1.484	47.5	65.43	1.223	25.5	35.13	1.025	3.5	4.82
1.476	47.0	64.75	1.218	25.0	34.44	1.021	3.0	4.13
1.469	46.5	64.06	1.213	24.5	33.75	1.017	2.5	3.44

DENSITY OF STRONG ACIDS AT 15° IN VACUO

(According to LUNGE, ISLER, NAEF, and MARCHLEWSKY)*

Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight			Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight	
	HCl	HNO_3	H_2SO_4		HNO_3	H_2SO_4
1.000	0.16	0.10	0.09	1.235	37.51	31.70
1.005	1.15	1.00	0.95	1.240	38.27	32.28
1.010	2.14	1.90	1.57	1.245	39.03	32.86
1.015	3.12	2.80	2.30	1.250	39.80	33.43
1.020	4.13	3.70	3.03	1.255	40.56	34.00
1.025	5.15	4.60	3.76	1.260	41.32	34.57
1.030	6.15	5.50	4.49	1.265	42.08	35.14
1.035	7.15	6.38	5.23	1.270	42.85	35.71
1.040	8.16	7.26	5.96	1.275	43.62	36.29
1.045	9.16	8.13	6.67	1.280	44.39	36.87
1.050	10.17	8.99	7.37	1.285	45.16	37.45
1.055	11.18	9.84	8.07	1.290	45.93	38.03
1.060	12.19	10.67	8.77	1.295	46.70	38.61
1.065	13.19	11.50	9.47	1.300	47.47	39.19
1.070	14.17	12.32	10.19	1.305	48.24	39.77
1.075	15.16	13.14	10.90	1.310	49.05	40.35
1.080	16.15	13.94	11.60	1.315	49.88	40.93
1.085	17.13	14.73	12.30	1.320	50.69	41.50
1.090	18.11	15.52	12.99	1.325	51.51	42.08
1.095	19.06	16.31	13.67	1.330	52.34	42.66
1.100	20.01	17.10	14.35	1.335	53.17	43.20
1.105	20.97	17.88	15.03	1.340	54.04	43.74
1.110	21.92	18.66	15.71	1.345	54.90	44.28
1.115	22.86	19.44	16.36	1.350	55.76	44.82
1.120	23.82	20.22	17.01	1.355	56.63	45.35
1.125	24.78	20.99	17.66	1.360	57.54	45.88
1.130	25.75	21.76	18.31	1.365	58.45	46.41
1.135	26.70	22.53	18.96	1.370	59.36	46.94
1.140	27.66	23.30	19.61	1.375	60.27	47.47
1.145	28.61	24.07	20.26	1.380	61.24	48.00
1.150	29.57	24.83	20.91	1.385	62.21	48.53
1.155	30.55	25.59	21.55	1.390	63.20	49.06
1.160	31.52	26.35	22.19	1.395	64.22	49.59
1.165	32.49	27.11	22.83	1.400	65.27	50.11
1.170	33.46	27.87	23.47	1.405	66.37	50.63
1.175	34.42	28.62	24.12	1.410	67.47	51.15
1.180	35.39	29.37	24.76	1.415	68.60	51.66
1.185	36.31	30.12	25.40	1.420	69.77	52.15
1.190	37.23	30.87	26.04	1.425	70.95	52.63
1.195	38.16	31.60	26.68	1.430	72.14	53.11
1.200	39.11	32.34	27.32	1.435	73.35	53.59
1.205		33.07	27.95	1.440	74.64	54.07
1.210		33.80	28.58	1.445	75.94	54.55
1.215		34.53	29.21	1.450	77.24	55.03
1.220		35.26	29.84	1.455	78.56	55.50
1.225		36.01	30.48	1.460	79.94	55.97
1.230		36.76	31.11	1.465	81.38	56.43

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* Lunge-Berl. *Chem. techn. Untersuchungsmethoden.*

DENSITY OF STRONG ACIDS AT 15° IN VACUO — *Continued*

Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight		Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight	Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight
	HNO_3	H_2SO_4		H_2SO_4		H_2SO_4
1.470	82.86	56.90	1.610	69.56	1.750	81.56
1.475	84.41	57.37	1.615	70.00	1.755	82.00
1.480	86.01	57.83	1.620	70.42	1.760	82.44
1.485	87.66	58.28	1.625	70.85	1.765	83.01
1.490	89.86	58.74	1.630	71.27	1.770	83.51
1.495	91.56	59.22	1.635	71.70	1.775	84.02
1.500	94.04	59.70	1.640	72.12	1.780	84.50
1.505	96.34	60.18	1.645	72.55	1.785	85.10
1.510	98.05	60.65	1.650	72.96	1.790	85.70
1.515	99.02	61.12	1.655	73.40	1.795	86.30
1.520	99.62	61.59	1.660	73.81	1.800	86.92
1.525		62.06	1.665	74.24	1.805	87.60
1.530		62.53	1.670	74.66	1.810	88.30
1.535		63.00	1.675	75.08	1.815	89.16
1.540		63.43	1.680	75.50	1.820	90.05
1.545		63.85	1.685	75.94	1.825	91.00
1.550		64.26	1.690	76.38	1.830	92.10
1.555		64.67	1.695	76.76	1.835	93.56
1.560		65.20	1.700	77.17	1.840	95.60
1.565		65.65	1.705	77.60	1.8405	95.95
1.570		66.09	1.710	78.04	1.8410	96.38
1.575		66.53	1.715	78.48	1.8415	97.35
1.580		66.95	1.720	78.92	1.8410	98.20
1.585		67.40	1.725	79.36	1.8405	98.52
1.590		67.83	1.730	79.80	1.8400	98.72
1.595		68.26	1.735	80.24	1.8395	98.77
1.600		68.70	1.740	80.68	1.8390	99.12
1.605		69.13	1.745	81.12	1.8385	99.31

DENSITY OF POTASSIUM AND SODIUM HYDROXIDE SOLUTIONS AT 15° C

Specific Gravity	Per Cent KOH	Per Cent NaOH	Specific Gravity	Per Cent KOH	Per Cent NaOH
1.007	0.9	0.59	1.252	27.0	22.50
1.014	1.7	1.20	1.263	28.2	23.50
1.022	2.6	1.65	1.274	28.9	24.48
1.029	3.5	2.50	1.285	29.8	25.50
1.037	4.5	3.22	1.297	30.7	26.58
1.045	5.6	3.79	1.308	31.8	27.65
1.052	6.4	4.50	1.320	32.7	28.83
1.060	7.4	5.20	1.332	33.7	30.00
1.067	8.2	5.86	1.345	34.9	31.20
1.075	9.2	6.58	1.357	35.9	32.50
1.083	10.1	7.30	1.370	36.9	33.73
1.091	10.9	8.07	1.383	37.8	35.00
1.100	12.0	8.78	1.397	38.9	36.36
1.108	12.9	9.50	1.410	39.9	37.65
1.116	13.8	10.30	1.424	40.9	39.06
1.125	14.8	11.06	1.438	42.1	40.47
1.134	15.7	11.90	1.453	43.4	42.02
1.142	16.5	12.69	1.468	44.6	43.58
1.152	17.6	13.50	1.483	45.8	45.16
1.162	18.6	14.35	1.498	47.1	47.73
1.171	19.5	15.15	1.514	48.3	48.41
1.180	20.5	16.00	1.530	49.4	50.10
1.190	21.4	16.91	1.546	50.6	.....
1.200	22.4	17.81	1.563	51.9	.....
1.210	23.3	18.71	1.580	53.2	.....
1.220	24.2	19.65	1.597	54.5	.....
1.231	25.1	20.69	1.615	55.9	.....
1.241	26.1	21.55	1.634	57.5	.....

DENSITY OF AMMONIA SOLUTIONS AT 15° C

(According to Lunge and Wiernik)*

Specific Gravity	Per Cent NH_3	Specific Gravity	Per Cent NH_3
1.000	0.00	0.940	15.63
0.998	0.45	0.938	16.22
0.996	0.91	0.936	16.82
0.994	1.37	0.934	17.42
0.992	1.84	0.932	18.03
0.990	2.31	0.930	18.64
0.988	2.80	0.928	19.25
0.986	3.30	0.926	19.87
0.984	3.80	0.924	20.49
0.982	4.30	0.922	21.12
0.980	4.80	0.920	21.75
0.978	5.30	0.918	22.39
0.976	5.80	0.916	23.03
0.974	6.30	0.914	23.68
0.972	6.80	0.912	24.33
0.970	7.31	0.910	24.99
0.968	7.82	0.908	25.65
0.966	8.33	0.906	26.31
0.964	8.84	0.904	26.98
0.962	9.35	0.902	27.65
0.960	9.91	0.900	28.33
0.958	10.47	0.898	29.01
0.956	11.03	0.896	29.69
0.954	11.60	0.894	30.37
0.952	12.17	0.892	31.05
0.950	12.74	0.890	31.75
0.948	13.31	0.888	32.50
0.946	13.88	0.886	33.25
0.944	14.46	0.884	34.10
0.942	15.04	0.882	34.95

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* Lunge-Berl. *Chem. techn. Untersuchungsmethoden.*

CHEMICAL FACTORS*

Sought	Found	Factor	Log
Ag	AgBr	0.5744	9.7593
	AgCl	0.7526	9.8766
	AgCN	0.8058	9.9062
	AgI	0.4595	9.6622
	$AgNO_3$	0.6350	9.8028
	Ag_2O	0.9310	9.9689
	Ag_2S	0.8706	9.9398
	Ag_3PO_4	0.7731	9.8882
	$Ag_4P_2O_7$	0.7125	9.8528
Ag_2O	AgCl	0.8084	9.9076
Al	Al_2O_3	0.5291	9.7236
	$AlPO_4$	0.2210	9.3446
Al_2O_3	$AlPO_4$	0.4178	9.6210
AlF_3	CaF_2	0.7170	9.8555
$AlCl_3$	Al_2O_3	2.616	0.4177
$Al_2(SO_4)_3$	Al_2O_3	3.356	0.5257
$Al_2(SO_4)_3.18,H_2O$	Al_2O_3	6.537	0.8154
As	As_2O_3	0.7575	9.8794
	As_2O_5	0.6521	9.8143
	As_2S_3	0.6091	9.7847
	As_2S_5	0.4832	9.6841
	I_2	0.2953	9.4703
	$Mg_2As_2O_7$	0.4827	9.6837
	$Mg_2P_2O_7$	0.6731	9.8281
	$(NH_4MgAsO_4)_2 H_2O$	0.3939	9.5953
As_2O_3	As_2O_5	0.8609	9.9349
	As_2S_3	0.8041	9.9053
	As_2S_5	0.6378	9.8047
	$2I_2$	0.3900	9.5909
	$Mg_2As_2O_7$	0.6372	9.8043
	$Mg_2P_2O_7$	0.8887	9.9487
	$(NH_4MgAsO_4)_2 H_2O$	0.5199	9.7160
AsO_3	As_2S_3	0.9992	9.9996
	As_2S_5	0.7926	9.8991
	$Mg_2As_2O_7$	0.7919	9.8987
AsO_3	$Mg_2P_2O_7$	1.104	0.0430
	$(NH_4MgAsO_4)_2 H_2O$	0.6460	9.8103
As_2O_5	As_2S_3	0.9341	9.9704
	As_2S_5	0.7410	9.8698
	$2I_2$	0.4529	9.6560
	$Mg_2As_2O_7$	0.7403	9.8694
	$Mg_2P_2O_7$	1.032	0.0138
	$(NH_4MgAsO_4)_2 H_2O$	0.6040	9.7810
AsO_4	As_2S_3	1.129	0.0528
	As_2S_5	0.8957	9.9522
	I_2	0.5473	9.7383
	$Mg_2As_2O_7$	0.8949	9.9518
	$Mg_2P_2O_7$	1.2477	0.0962
	$(NH_4MgAsO_4)_2. H_2O$	0.7301	9.8634
Au	$AuCl_3$	0.6496	9.8126
	$HAuCl_4.4H_2O$	0.4785	9.6799
	$KAu(CN)_4.H_2O$	0.5500	9.7403
B	B_2O_3	0.3107	9.4924
	KBF_4	0.08593	8.9342
	H_3BO_3	0.1750	9.2430
	$Na_2B_4O_7.10H_2O$	0.1135	9.0549
B_2O_3	KBF_4	0.2766	9.4418
	H_3BO_3	0.5630	9.7505
	$Na_2B_4O_7.10H_2O$	0.3652	9.5625
BO_2	B_2O_3	1.229	0.0898
BO_3	B_2O_3	1.689	0.2277
B_4O_7	B_2O_3	1.115	0.0472
Ba	$BaCl_2.2H_2O$	0.5621	9.7498
	$BaCO_3$	0.6961	9.8426
	$BaCrO_4$	0.5422	9.7341
	$BaSO_4$	0.5885	9.7697
	$BaSiF_6$	0.4916	9.6916
BaO	$BaCO_3$	0.7771	9.8905
	$BaCrO_4$	0.6053	9.7820
	$BaSO_4$	0.6570	9.8176
	$BaSiF_6$	0.5489	9.7395

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* The use of the table will be illustrated by two examples. (1) What weight of silver corresponds to p grams of silver bromide? Look up Ag in the column "Sought" and AgBr in the column "Found." For computation with a slide rule, use column 3, $p \times 0.5744$ = weight of Ag. With logarithms, $\log p + 9.7592$ = log weight of Ag. (2) What weight of silver bromide corresponds to q grams of silver? Use the same factor as before but *divide* by it or *subtract* the logarithm.

Strictly speaking, the logarithm in the above case is not 9.7592 but 9.7592 − 10 or $\overline{1}.7592$, in which the characteristic is a negative number and the mantissa a positive fraction.

In computing the weight of silver bromide instead of subtracting the logarithm 9.7592 it is more convenient to add the co-logarithm 0.2407 which is obtained quickly by subtracting each digit of 9.7592 from 9 except the last one which is subtracted from 10. It gives the logarithm of $\frac{1}{0.5744} = 0.2408$.

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
BaO_2	Ba	1.233	0.0909
	$BaCrO_4$	0.6685	9.8251
	$BaSO_4$	0.7256	9.8607
$BaCO_3$	$BaSO_4$	0.8458	9.9272
$BaCl_2.2H_2O$	$BaSO_4$	1.047	0.0198
$BaCrO_4$	$BaSO_4$	1.085	0.0356
BaF_2	$BaSiF_6$	0.6276	9.7977
$Ba(NO_3)_2$	$BaSO_4$	1.120	0.0491
$Ba_3(PO_4)_2$	$BaSO_4$	0.8599	9.9345
BaS	$BaSO_4$	0.7258	9.8608
Be	BeO	0.3605	9.5569
BeO	$BeCl_2$	0.3130	9.4956
BeO	$BeSO_4.4H_2O$	0.1412	9.1500
Bi	Bi_2O_3	0.8970	9.9528
	BiOCl	0.8024	9.9044
	$BiPO_4$	0.6874	9.8372
	Bi_2S_3	0.8129	9.9101
	$BiAsO_4$	0.6006	9.7786
Bi_2O_3	Bi	1.115	0.0472
	BiOCl	0.8946	9.9516
	$BiPO_4$	0.7663	9.8844
	Bi_2S_3	0.9063	0.9573
	$BiAsO_4$	0.6696	9.8258
	$BiONO_3$	0.8118	9.9095
	$Bi(NO_3)_3.5H_2O$	0.4803	9.6815
Br	Ag	0.7408	9.8697
	AgBr	0.4256	9.6290
	AgCl	0.5576	9.7463
	HBr	0.9874	9.9945
BrO_3	Ag	1.186	0.0740
	AgBr	0.6812	9.8332
Br_2O_5	Ag	1.111	0.0459
	AgBr	0.6386	9.8052
C	CO_2	0.2727	9.4357
	$BaCO_3$	0.0608	8.7839
CO_2	$BaCO_3$	0.2229	9.3482
	BaO	0.2869	9.4577
	$Ba(HCO_3)_2$	0.3395	9.5309
	$CaCO_3$	0.4396	9.6430
	$Ca(HCO_3)_2$	0.5431	9.7349
	CaO	0.7844	9.8946
	CO_3	0.7333	9.8653
	Cs_2CO_3	0.1351	9.1307
	$FeCO_3$	0.3801	9.5799
	$Fe(HCO_3)_2$	0.4948	9.6944
	K_2CO_3	0.3184	9.5029
	$KHCO_3$	0.4395	9.6430
	Li_2CO_3	0.5956	9.7749
	$LiHCO_3$	0.6476	9.8113
CO_2	$MgCO_3$	0.5218	9.7175
	$Mg(HCO_3)_2$	0.6014	9.7791
	MgO	1.091	0.0379
	$MnCO_3$	0.3828	9.5831
	$Mn(HCO_3)_2$	0.4973	9.6960
	Na_2CO_3	0.4151	9.6182
	$NaHCO_3$	0.5238	9.7192
	Na_2O	0.7098	9.8512
	$(NH_4)_2CO_3$	0.4580	9.6608
	$PbCO_3$	0.1647	9.2166
	Rb_2CO_3	0.1907	9.2801
	$Rb(HCO_3)$	0.3005	9.4778
	$SrCO_3$	0.2980	9.4745
	$Sr(HCO_3)_2$	0.4198	9.6230
	SrO	0.4251	9.6285
	$ZnCO_3$	0.3509	9.5452
CO_3	CO_2	1.364	0.1347
Ca	$CaCl_2$	0.3612	9.5577
	$CaCO_3$	0.4005	9.6025
	$CaC_2O_4.H_2O$	0.2743	9.4383
	CaC_2O_4	0.3129	9.4954
	CaF_2	0.5133	9.7103
	CaO	0.7146	9.8541
	$CaSO_4$	0.2944	9.4689
	CO_2	0.9109	9.9595
CaO	$CaCO_3$	0.5603	9.7484
	$CaC_2O_4.H_2O$	0.3839	9.5842
	CaC_2O_4	0.4378	9.6413
	CaF_2	0.7182	9.8563
	$Ca(HCO_3)_2$	0.3459	9.5389
	$Ca(H_2PO_4)_2.H_2O$	0.2204	9.3471
	$Ca_2P_2O_7$	0.2206	9.3436
	$Ca(HSO_3)_2$	0.2773	9.4430
	$Ca_3(PO_4)_2$	0.5421	9.7341
	$CaSO_3$	0.4667	9.6691
	$CaSO_4$	0.4120	9.6149
	$CaSO_4.2H_2O$	0.3257	9.5128
	CO_2	1.274	9.1053
$Ca_3(PO_4)_2$	$Mg_2P_2O_7$	1.393	0.1440
CaS	$BaSO_4$	0.3091	9.4901
$CaSO_4$	$BaSO_4$	0.5832	9.7658
$CaSO_4.2H_2O$	CaO	3.071	0.4872
CaF_2	$CaSO_4$	0.5735	9.7586
Cb	Cb_2O_5	0.6999	9.8451
Cd	CdO	0.8754	9.9422
	CdS	0.7780	9.8910
	$CdSO_4$	0.5392	9.7317
CdO	CdS	0.8888	9.9488
	Cd	1.142	0.0578
	$CdSO_4$	0.6159	9.7895

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
CdS	Cd	1.2853	0.1090
	CdO	1.1252	0.0512
	$CdSO_4$	0.6930	9.8407
Ce	$Ce(NO_3)_4$	0.3610	9.5575
	Ce_2O_3	0.8538	9.9313
	CeO_2	0.8141	9.9107
	$Ce(SO_4)_3$	0.4930	9.6929
Ce_2O_3	CeO_2	0.9536	9.9794
Cl	Ag	0.3287	9.5168
	AgCl	0.2474	9.3934
	$AgNO_3$	0.2087	9.3195
	HCl	0.9724	9.9879
	I	0.2794	9.4462
	KCl	0.4756	9.6772
	MnO_2	0.8158	9.9116
	NaCl	0.6066	9.7829
	NH_4Cl	0.6628	9.8214
	RbCl	0.2933	9.4673
ClO_3	AgCl	0.5823	9.7651
	KCl	1.119	0.0490
	NaCl	1.428	0.1546
ClO_4	AgCl	0.6939	0.8413
	KCl	1.334	0.1251
	NaCl	1.701	0.2308
CN	AgCN	0.1943	9.2884
	Ag	0.2411	9.3822
	KCN	0.3999	9.6020
	NaCN	0.5313	9.7253
	HCN	0.9627	9.9835
CNS	AgCNS	0.3500	9.5440
	$Cu_2(CNS)_2$	0.4774	9.6789
	$BaSO_4$	0.2488	9.3959
	KCNS	0.5974	9.7765
	NH_4CNS	0.7632	9.8825
Co	$Co(NO_3)_2.6H_2O$	0.2026	9.3066
	$K_3Co(NO_2)_6$	0.1304	9.1152
	CoO	0.7866	9.8957
	Co_3O_4	0.7344	9.8659
	$CoSO_4$	0.3804	9.5802
	$CoSO_4.7H_2O$	0.2097	9.3216
CoO	Co	1.2713	0.1043
	$Co(NO_3)_2.6H_2O$	0.2575	9.4109
	$K_3Co(NO_2)_6$	0.1657	9.2194
	Co_3O_4	0.9336	9.9702
	$CoSO_4$	0.4836	9.6844
	$CoSO_4.7H_2O$	0.2667	9.4259
Cr	$BaCrO_4$	0.2052	9.3125
	Cr_2O_3	0.6842	9.8352

Sought	Found	Factor	Log
Cr	$PbCrO_4$	0.1609	9.2067
	$K_2Cr_2O_7$	0.3535	9.5484
	K_2CrO_4	0.2678	9.4278
Cr_2O_3	$BaCrO_4$	0.3000	9.4771
	$PbCrO_4$	0.2352	9.3715
	CrO_3	0.7602	9.8809
Cr	$BaCrO_4$	0.3947	9.5963
	Cr_2O_3	1.3158	0.1192
	$PbCrO_4$	0.3095	9.4907
	K_2CrO_4	0.5150	9.7118
	$K_2Cr_2O_7$	0.6800	9.8325
CrO_4	$BaCrO_4$	0.4578	9.6607
	Cr_2O_3	1.5263	0.1837
	$PbCrO_4$	0.3589	9.5550
Cs	CsCl	0.7893	9.8973
	Cs_2O	0.9432	9.9746
	Cs_2CO_3	0.8157	9.9116
	Cs_2SO_4	0.7340	9.8654
	Cs_2PtCl_6	0.3945	9.5960
Cs_2O	CsCl	0.8370	0.9227
	Cs_2CO_3	0.8650	9.9370
	Cs_2SO_4	0.7786	9.8913
	Cs_2PtCl_6	0.4182	9.6214
Cu	Cu_2O	0.8882	9.9485
	CuO	0.7989	9.9025
	Cu_2S	0.7986	9.9023
	$Cu_2(CNS)_2$	0.5226	9.7181
	CuSO	0.3982	9.6001
	$CuSO_4.5H_2O$	0.2546	9.4058
CuO	Cu	1.252	0.0975
	Cu_2O	1.113	0.0463
	Cu_2S	0.9996	9.9998
	$Cu_2(CNS)_2$	0.6541	9.8156
	$CuSO_4$	0.4985	9.6976
	$CuSO_4.5H_2O$	0.3186	9.5032
Er_2O_3	Er	1.145	0.0589
Er	Er_2O_3	0.8732	9.9411
F	$BaSiF_6$	0.4080	9.6107
	CaF_2	0.4866	9.6872
	$CaSO_4$	0.2791	9.4457
	HF	0.9496	9.9776
	H_2SiF_6	0.7913	9.8983
	K_2SiF_6	0.5176	9.7140
	NaF	0.4524	9.6555
	SiF_4	0.7302	9.8634
Fe	Fe_2O_3	0.6994	9.8447
	$FeCl_2$	0.4405	9.6440
	$FeCl_3.6H_2O$	0.2066	9.3152

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
Fe	$Fe(HCO_3)_2$	0.3140	9.4969
	FeO	0.7773	9.8906
	Fe_3O_4	0.7236	9.8595
	$FePO_4$	0.3701	9.5683
	FeS	0.6352	9.8029
	$FeSO_4$	0.3676	9.5654
	$FeSO_4.7H_2O$	0.2009	9.3029
	$FeSO_4(NH_4)_2SO_4.6H_2O$	0.1424	9.1536
FeO	Fe	1.287	0.1094
	$FeCO_3$	0.6202	9.7925
	$Fe(HCO_3)_2$	0.4039	9.6063
	Fe_2O_3	0.8998	9.9542
	$FePO_4$	0.4761	9.6777
	FeS	0.8172	9.9123
	$FeSO_4$	0.4729	9.6747
	$FeSO_4.7H_2O$	0.2584	9.4123
	$FeSO_4(NH_4)_2SO_4.6H_2O$	0.1832	9.2630
Fe_2O_3	Fe	1.430	0.1553
	$FeCl_3$	0.4922	9.6922
	$FeCO_3$	0.6892	9.8383
	Fe_3O_4	1.035	0.0149
	$FePO_4$	0.5292	9.7237
	FeS	0.9082	9.9582
	FeS_2	0.6655	9.8231
	$Fe_2(SO_4)_3$	0.3993	9.6013
	$(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$	0.1656	9.2190
FeS_2	$BaSO_4$	0.2570	9.4099
H	H_2O	0.1119	9.0488
H_3BO_3	B_2O_3	1.776	0.2495
HBr	Ag	0.7505	9.8754
	AgBr	0.4309	9.6344
HCl	Ag	0.3380	9.5290
	AgCl	0.2544	9.4056
	$CaCO_3$	0.7288	9.8626
	KCl	0.4891	9.6894
	K_2O	0.7743	9.8889
	NaCl	0.6239	9.7951
	Na_2O	1.176	0.0705
	NH_4Cl	0.6817	9.8335
	$SnCl_4$	0.5600	9.7480
	Na_2CO_3 methyl orange	0.6881	9.8377
	$Na_2C_2O_4$ standardization	0.5442	9.7358
HF	$BaSiF_6$	0.4296	9.6331
	CaF_2	0.5126	9.7098
	$CaSO_4$	0.2939	9.4682
HF	F	1.053	0.0224
	K_2SiF_6	0.5449	9.7363
HI	Ag	1.186	0.0742
	AgI	0.5448	9.7362
	Pd	2.398	0.3799
	PdI_2	0.7097	9.8510
HNO_2	$AgNO_2$	0.3055	9.4850
	NO	1.567	0.1950
HNO_3	KNO_3	0.6233	9.7947
	N	4.498	0.6530
	$NaNO_3$	0.7413	9.8700
	NH_3	3.701	0.5683
	NH_4Cl	1.178	0.0711
	$(NH_4)_2PtCl_6$	0.2838	9.4530
	NO	2.100	0.3222
	N_2O_3	1.658	0.2196
	N_2O_4	1.370	0.1367
	N_2O_5	1.167	0.0671
	$C_{20}H_{16}N_4HNO_3$	0.1680	9.2252
	Pt	0.6457	9.8100
H_3PO_4	HPO_3	1.225	0.0881
	$H_4P_2O_7$	1.101	0.0457
	$Mg_2P_2O_7$	0.8806	9.9448
	P	3.159	0.4995
	P_2O_5	1.380	0.1399
$H_2PtCl_6.6H_2O$	Pt	2.654	0.4239
H_2S	$BaSO_4$	0.1460	9.1644
	CdS	0.2360	9.3729
	FeS	0.3877	9.5885
	S	1.063	0.0265
H_2SeO_3	Se	1.632	0.2126
H_2SiF_6	$BaSiF_6$	0.5157	9.7124
	$3CaF_2$	0.6149	9.7888
	F	1.264	0.1018
	2HF	3.601	0.5564
	6HF	1.200	0.0792
	K_2SiF_6	0.6541	9.8157
	SiF_4	1.384	0.1412
H_2SO_4	$Al_2(SO_4)_3$	0.8594	9.9342
	$Ba(OH)_2$	0.5719	9.7574
	$BaSO_4$	0.4200	9.6232
	$K_2Al_2(SO_4)_4.24H_2O$	0.4132	9.6162
	K_2O	1.041	0.0174
	KOH	0.8736	9.9413
	K_2SO_4	0.5625	9.7501
	Na_2CO_3	0.9252	9.9662
	$Na_2C_2O_4$	0.7318	9.8642

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
H_2SO_4	$(NH_4)_2SO_4$	0.7418	9.8703
Hg	Hg_2Cl_2	0.8498	9.9293
	$HgCl_2$	0.7388	9.8686
	HgO	0.9261	9.9666
	HgS	0.8620	9.9355
HCNS	AgCNS	0.3560	9.5515
	$Cu_2(CNS)_2$	0.4857	9.6864
	$BaSO_4$	0.2531	9.4033
Hg_2Cl_2	$SnCl_2$	2.486	0.3956
$HgCl_2$	Hg_2Cl_2	1.150	0.0607
	HgS	1.167	0.0671
HgO	Hg_2Cl_2	0.9176	9.9627
HgS	$Hg(CN)_2$	0.9210	9.9643
	$HgNO_3$	0.8860	9.9474
	$Hg(NO_3)_2$	0.7167	9.8554
	Hg_2O	1.115	0.0474
	HgO	1.074	0.0311
	$HgSO_4$	0.7843	9.8945
I	Ag	1.177	0.0706
	AgI	0.5406	9.7328
	KI	0.7645	9.8834
	Pd	2.379	0.3764
	PdI_2	0.7041	9.8476
	$Na_2S_2O_3.5H_2O$	0.5113	9.7087
	AgCl	0.8855	9.9472
In	In_2O_3	0.8271	9.9176
	In_2S_3	0.7047	9.8480
Ir	Ir_2O_3	0.8894	9.9491
K	KCl	0.5244	9.7197
	K_2O	0.8300	9.9191
	K_2SO_4	0.4487	9.6520
	$KClO_4$	0.2822	9.4505
	K_2PtCl_6	0.1609	9.2064
	Pt	0.4006	9.6027
KCl	Ag	0.6911	9.8396
	AgCl	0.5202	9.7162
	K_2SO_4	0.8557	9.9323
	$KClO_4$	0.5381	9.7309
	K_2PtCl_6	0.3067	9.4868
	Pt	0.7638	9.8830
K_2O	KCl	0.6317	9.8005
	K_2SO_4	0.5405	9.7328
	$KClO_4$	0.3399	9.5314
	K_2PtCl_6	0.1938	9.2873
	Pt	0.4826	9.6836
$KClO_3$	AgCl	0.8550	9.9320
	KCl	1.6438	0.2158
$KClO_4$	AgCl	0.9667	9.9853
	KCl	1.858	0.2691
KCN	AgCN	0.4863	9.6869
	$AgNO_3$ (Liebig method)	0.7665	9.8845
	AgCl	0.4542	9.6573
K_2SO_4	K	2.229	0.3481
	KCl	1.169	0.0679
	K_2O	1.850	0.2672
	K_2PtCl_6	0.3585	9.5545
	SO_3	2.177	0.3379
	$BaSO_4$	0.7465	9.8731
La	La_2O_3	0.8527	9.9308
Li	LiCl	0.1637	9.2140
	Li_2O	0.4643	9.6669
	Li_3PO_4	0.1797	9.2545
	Li_2SO_4	0.1262	9.1012
Li_2O	LiCl	0.3524	9.5470
	Li_2SO_4	0.2718	9.4342
	Li_3PO_4	0.3870	9.5877
Mg	MgO	0.6032	9.7804
	$MgSO_4$	0.2020	9.3054
	$Mg_2P_2O_7$	0.2184	9.3392
	$MgSO_4$	0.2020	9.3054
	$MgNH_4PO_4.H_2O$	0.1565	9.1946
	$MgNH_4PO_4.6H_2O$	0.0991	8.9961
MgO	$MgSO_4$	0.3349	9.5249
	$Mg_2P_2O_7$	0.3621	9.5588
	$MgCO_3$	0.4782	9.6796
	$MgNH_4PO_4.H_2O$	0.2595	9.4141
	$MgNH_4PO_4.6H_2O$	0.1643	9.2156
Mn	$MnCO_3$	0.4779	9.6793
	MnO	0.7744	9.8889
	Mn_2O_3	0.6959	9.8426
	Mn_3O_4	0.7203	9.8575
	$MnSO_4$	0.3638	9.5608
	$Mn_2P_2O_7$	0.3869	9.5876
	MnS	0.6314	9.8003
MnO	$MnCO_3$	0.6172	9.7904
	Mn_3O_4	0.9301	9.9685
	$MnSO_4$	0.4697	9.6719
	MnS	0.8153	9.9113
	$Mn_2P_2O_7$	0.4998	9.6988

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
Mo	MoO_3	0.6667	9.8239
	MoS_3	0.4995	9.6985
	MoS_2	0.5996	9.7779
	$PbMoO_4$	0.2615	9.4174
MoO_3	MoS_3	0.7492	9.8746
	$(NH_4)_2MoO_4$	0.7344	9.8659
	$(NH_4)_3PO_4.12MoO_3$	0.9205	9.9640
	$PbMoO_4$	0.3923	9.5936
N	HNO_3	0.2223	9.3470
	NO_2	0.3045	9.4835
	N_2O_3	0.3686	9.5665
	N_2O_4	0.3045	9.4835
	N_2O_5	0.2594	9.4140
	$NaNO_3$	0.1648	9.2169
	NH_3	0.8225	9.9151
	Pt	0.1435	9.1570
	NH_4Cl	0.2619	9.4181
Na	NaCl	0.3934	9.5949
	Na_2SO_4	0.3238	9.5103
	NaBr	0.2235	9.3493
	Na_2CO_3	0.4340	9.6375
	NaF	0.5476	9.7385
	$NaHCO_3$	0.2738	9.4374
	NaI	0.1534	9.1858
	Na_2O	0.7419	9.8704
	NaOH	0.5750	9.7597
	Na_2SO_4	0.3238	9.5103
$Na_2B_4O_7$	B_2O_3	1.443	0.1593
	H_3BO_3	0.8142	9.9107
$Na_2B_4O_7.10H_2O$	B_2O_3	2.738	0.4375
	H_3BO_3	1.540	0.1872
	KBF	0.7577	9.8795
NaBr	Ag	0.9539	9.9795
	AgBr	0.5480	9.7388
NaCl	Ag	0.5418	9.7338
	AgCl	0.4078	9.6105
	$AgNO_3$	0.3441	9.5367
	Na_2O	1.886	0.2756
NaF	CaF_2	1.076	0.0317
Na_2HAsO_3	$Mg_2As_2O_7$	1.095	0.0395
	I	0.6697	9.8259
Na_2HAsO_4	$Mg_2As_2O_7$	1.198	0.0785
	I	0.7328	9.8650
$NaHCO_3$	CO_2	1.909	0.2808
$NaHCO_3$	$KHC_4H_4O_6$	0.4465	9.6498
Na_2O	NaCl	0.5303	9.7245
	Na_2SO_4	0.4364	9.6399
	Na_2CO_3	0.5849	9.7671
	$NaHCO_3$	0.3690	9.5670
	Na_2HPO_4	0.4365	9.6400
	NaH_2PO_4	0.2582	9.4119
	$Na_2H_2P_2O_7$	0.2792	9.4459
	$NaHSO_3$	0.2979	9.4741
	$NaNO_3$	0.3647	9.5619
	NaOH	0.7748	9.8891
	Na_2SO_4	0.4364	9.6399
Na_2SO_3	$BaSO_4$	0.5401	9.7325
$Na_2S_2O_3$	$BaSO_4$	0.3387	9.5298
	$Na_2S_2O_3.5H_2O$	0.6371	9.8042
Na_2SO_4	$BaSO_4$	0.6086	9.7843
Nd	Nd_2O_3	0.8572	9.9332
NH_3	HNO_3	0.2704	9.4320
	H_2SO_4	0.3473	9.5407
	N	1.216	0.0849
	$NaNO_2$	0.2468	9.3923
	$NaNO_3$	0.2005	9.3021
	NH_4Cl	0.3184	9.5029
	$(NH_4)_2HPO_4$	0.2578	9.4113
	$(NH_4)H_2PO_4$	0.1480	9.1703
	$(NH_4)OH$	0.4860	9.6866
	$(NH_4)_2PtCl_6$	0.07670	8.8848
	$(NH_4)_2SO_4$	0.2578	9.4113
	N_2O_5	0.3153	9.4987
	Pt	0.1745	9.2418
NH_4	NH_3	1.059	0.0250
	NH_4Cl	0.3372	9.5279
	$(NH_4)_2PtCl_6$	0.08125	8.9099
	Pt	0.1848	9.2668
NH_4Cl	AgCl	0.3732	9.5719
	NH_3	3.141	0.4971
	$(NH_4)_2PtCl_6$	0.2410	1.3820
	Pt	0.5482	9.7389
$(NH_4)_2SO_4$	$BaSO_4$	0.5661	9.7529
Ni	NiO	0.7858	9.8953
	$NiC_8H_{14}N_4O_4$	0.2032	9.3079
	$NiSO_4$	0.3792	9.5788
	$Ni(NO_3)_2.6H_2O$	0.2018	9.3049
	$Ni_2SO_4.7H_2O$	0.2089	9.3200
NO_3	NO	2.066	0.3152
	NH_3	3.640	0.5612

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
NO_3	NH_4Cl	1.159	0.0641
	$(NH_4)_2PtCl_6$	0.2793	9.4461
	Pt	0.6354	9.8030
	$C_{20}H_{17}N_5O_3$	0.1653	9.2182
N_2O_5	NO	1.800	0.2552
	NH_3	3.171	0.5012
	NH_4Cl	1.010	0.0041
	$(NH_4)_2PtCl_6$	0.2433	9.3861
	Pt	0.5534	9.7430
	$C_{20}H_{17}N_5O_3$	0.1440	9.1582
NO_2	NO	1.533	0.1856
N_2O_3	NO	1.267	0.1026
Os	OsO_4	0.7489	9.8744
P	$Mg_2P_2O_7$	0.2787	9.4452
	$P_2O_5.24MoO_3$	0.0173	8.2368
	$(NH_4)_3PO_4.12MoO_3$	0.0165	8.2184
	P_2O_5	0.4369	9.6404
	$MgNH_4PO_4.H_2O$	0.1996	9.3003
	$MgNH_4PO_4.6H_2O$	0.1262	9.1018
	$PbMoO_4$	0.00704	7.8475
PO_4	$Mg_2P_2O_7$	0.8535	9.9312
	$P_2O_5.24MoO_3$	0.05283	8.7229
	$(NH_4)_3PO_4.12MoO_3$	0.05063	8.7044
P_2O_5	$Mg_2P_2O_7$	0.6379	9.8048
	$P_2O_5.24MoO_3$	0.03947	8.5963
	$(NH_4)_3PO_4.12MoO_3$	0.03785	8.5780
	$MgNH_4PO_4.H_2O$	0.4571	9.6600
	$MgNH_4PO_4.6H_2O$	0.2894	9.4615
Pb	PbO	0.9283	9.9677
	PbO_2	0.8662	9.9376
	PbS	0.8659	9.9375
	$PbSO_4$	0.6831	9.8345
	$PbCrO_4$	0.6410	9.8068
	$PbCl_2$	0.7449	9.8721
	$PbMoO_4$	0.5642	9.7515
PbO	PbO_2	0.9331	9.9699
	PbS	0.9328	9.9698
	$PbSO_4$	0.7359	9.8668
	$PbCrO_4$	0.6905	9.8392
	$PbCl_2$	0.8025	9.9044
	$PbCO_3$	0.8353	9.9219
	$Pb(NO_3)_2$	0.6738	9.8285
PbS	$PbSO_4$	0.7889	9.8970
	Pb	1.155	0.0626

Sought	Found	Factor	Log
PbS	PbO	1.072	0.0302
	$BaSO_4$	1.025	0.0109
$PbSO_4$	$BaSO_4$	1.299	0.1137
	$Pb(C_2H_3O_2)_2.3H_2O$	0.7995	9.9028
	$(PbCO_3)_2.Pb(OH)_2$	1.173	0.0693
Rb	$AgCl$	0.5961	9.7753
	Cl	2.410	0.3820
	$RbCl$	0.7067	9.8492
	Rb_2CO_3	0.7402	9.8693
	Rb_2O	0.9144	9.9611
	Rb_2SO_4	0.6403	9.8064
	Rb_2PtCl_6	0.2952	9.4701
Rb_2O	$RbCl$	0.7729	9.8881
	Rb_2SO_4	0.7001	9.8452
$RbCl$	Rb_2PtCl_6	0.4178	9.6209
S	$BaSO_4$	0.1374	9.1379
	H_2S	0.9408	9.9735
	H_2SO_4	0.3270	9.5145
	FeS	0.3648	9.5621
	FeS_2	0.5346	9.7280
	Na_2S	0.4108	9.6136
SO_2	$BaSO_4$	0.2745	9.4385
	S	1.998	0.3007
SO_3	$BaSO_4$	0.3430	9.5353
	$CaSO_4$	0.5881	9.7695
	H_2SO_4	0.8163	9.9119
	K_2SO_4	0.4595	9.6623
	Na_2SO_4	0.5635	9.7510
SO_4	$BaSO_4$	0.4115	9.6144
Sb	$KSbOC_4H_4O_6.\frac{1}{2}H_2O$	0.3648	9.5620
	$SbCl_3$	0.5339	9.7275
	Sb_2O_3	0.8356	9.9220
	Sb_2O_5	0.7528	9.8767
	Sb_2O_4	0.7921	9.8988
	Sb_2S_3	0.7169	9.8555
	Sb_2S_5	0.6030	9.7803
Sb_2O_3	Sb_2O_4	0.9479	9.9768
	Sb_2S_3	0.8580	9.9335
	Sb_2S_5	0.7218	9.8584
SeO_2	Se	1.405	0.1474
SeO_3	Se	1.606	0.2058
Si	SiO_2	0.4672	9.6695
	SiO_3	0.3689	9.5669

CHEMICAL FACTORS — *Concluded*

Sought	Found	Factor	Log
i	SiO_4	0.3048	9.4840
iO_3	SiO_2	1.266	0.1025
iO_4	SiO_2	1.532	0.1854
n	SnO_2	0.7877	9.8963
	SnO	0.8812	9.9451
	$SnCl_2$	0.6261	9.7967
	$SnCl_2.2H_2O$	0.5260	9.7210
r	SrO	0.8456	9.9272
	$SrCO_3$	0.5936	9.7735
	$SrSO_4$	0.4770	9.6785
	$Sr(NO_3)_2$	0.4140	9.6170
rO	$SrCO_3$	0.7020	9.8463
	$SrSO_4$	0.5641	9.7514
	$Sr(NO_3)_2$	0.4896	9.6899
Ta	$TaCl_5$	0.5057	9.7039
	Ta_2O_5	0.8194	9.9135
Te	TeO_2	0.7994	9.9027
	TeO_3	0.7265	9.8612
Th	ThO_2	0.8788	9.9439
	$Th(NO_3)_4.6H_2O$	0.3947	9.5962
	$ThCl_4$	0.6207	9.7929
ThO_2	$Th(NO_3)_4.6H_2O$	0.4490	9.6523
Ti	TiO_2	0.5996	9.7778
Tl	$TlCl$	0.8522	9.9305
Tl	Tl_2CO_3	0.8720	9.9405
	TlI	0.6169	9.7902
	$TlNO_3$	0.7672	9.8849
	Tl_2O	0.9623	9.9833
	Tl_2CrO_4	0.7789	9.8915
	Tl_2SO_4	0.8097	9.9083
	$TlHSO_4$	0.6780	9.8312
Tl_2O	Tl_2PtCl_6	0.5200	9.7161
U	U_3O_8	0.8480	9.9283
	UO_2	0.8815	9.9452
	$(UO_2)_2P_2O_7$	0.6667	9.8240
V	V_2O_5	0.5602	9.7483
	V_2O_4	0.6142	9.7883
W	WO_3	0.7931	9.8993
	$PbWO_4$	0.4435	9.6469
Yt	Yt_2O_3	0.7875	9.8962
Yb	Yb_2O_3	0.8785	9.9437
Zn	ZnO	0.8034	9.9049
	$ZnNH_4PO_4$	0.3663	9.5639
	$Zn_2P_2O_7$	0.4290	9.6324
	ZnS	0.6710	9.8267
ZnO	ZnS	0.8352	9.9218
	$ZnNH_4PO_4$	0.4561	9.6590
	$Zn_2P_2O_7$	0.5340	9.7275
Zr	ZrO_2	0.7403	9.8694

Natural Numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

Natural Numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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